CHAPTER III

EFFECT OF CATIONIC GEMINI SURFACTANTS ON THE HYDROLYSIS OF CARBOXYLATE AND PHOSPHATE ESTERS USING HYDROXAMATE IONS

The kinetics of the hydrolysis of p-nitrophenyl acetate (PNPA) and p-nitrophenyl diphenyl phosphate (PNPDPP) by hydroxamate ions mediated by gemini surfactants with quaternary ammonium bromide (16-n-16,2Br\textsuperscript{−}, n = 3, 4, 6, 12) and pyridinium chloride (12py-n-py12, 2Cl\textsuperscript{−}, n = 3, 4) head group have been investigated at 27°C. The Gemini surfactant with pyridinium head group, 12-py-4-py12,2Cl\textsuperscript{−} (tetramethylene-1,4 bis dodecylpyridinium chloride) shows large rate acceleration effect, than that with ammonium head group, 16-12-16,2Br\textsuperscript{−}, relative to those in water. The apparent pK\textsubscript{a} of the hydroxamic acids have been determined in the presence of gemini surfactants. Catalytic system N-phenylbenzohydroxamate/12py-4-py12,2Cl\textsuperscript{−} demonstrated over ~1590-fold and ~255-fold rate enhancement in the hydrolysis of PNPA and PNPDPP respectively, for the identical reaction performed in buffer aqueous media at 27°C. The second order rate constant and binding constants for reactions were determined employing pseudophase model for micellar catalysis.

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CHAPTER III: EFFECT OF CATIONIC GEMINI SURFACTANTS ON THE HYDROLYSIS OF CARBOXYLATE AND PHOSPHATE ESTERS USING HYDROXAMATE IONS

3.0 INTRODUCTION

Gemini surfactants are composed of two monomeric surfactant molecules connected by a spacer chain. They constitute a new class of amphiphilic molecules having its own distinct behaviour. Since their first systematic studies over a decade ago, gemini surfactants have been the subject of intensive research. 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.

In recent years, considerable efforts has been made to design and synthesize new form of gemini surfactants having the required properties, to elucidate the relationship between the molecular structures of geminis and their aggregate morphology in aqueous solution and to understand the factor underlying the variation of their thermodynamic properties with the length of the side chains and spacers. Recently Borse et al. investigated the aggregation behavior of some novel class of gemini surfactants containing monoethanol and diethanol, e.g. 12-4-12 DMA and 12-4-12 DEA, head groups. As a new generation surfactants, gemini surfactants have a great interest in recent years. However, application of them to micellar or metallomicellar catalysis as a model to mimic the enzymes and
Metalloenzymes is not explored extensively. Surprisingly, there appeared less report on the kinetics of the esterolytic reaction in the presence of gemini surfactants.

Current interest in studying the reactions of α-nucleophiles has received major importance in many applications of this highly reactive species. For example, in the development of protocols for environmental decomposition of sites polluted with organophosphorus insecticides, α-nucleophiles such as oximates, hydroxamates, hydroperoxide, iodosobenzolate and hydroxyl-benzotriazoles and tetrazole, etc. has been demonstrated to be highly effective. The need to develop efficient means to destroy stockpiles of organophosphorus nerve agents have led a number of groups to investigate different approaches towards enhancing decomposition of these agents, α-nucleophiles can accelerate these decomposition. In this connection, hydroxamate ion attracts a special interest. Hydroxamate ions (III) act as good deacylating and dephosphorylating agents. They are considered as good α-nucleophiles due to the presence of unshared pair of electrons adjacent to the nucleophilic center. In this regard, we have been studying the esterolytic cleavage of carboxylate and phosphate esters using hydroxamate ions in cationic micellar media over the last few years.

3.1 REVIEW OF THE EARLIER WORK

The unusual characteristics of gemini surfactants makes it a very interesting topic of research. A number of studies have reported their versatile synthesis as well as their wide range of physicochemical properties, most of which have focused attention on the micellization and micellar structure. However, the reaction kinetics of esters catalyzed by gemini cationic surfactant micelles have
seldom been reported. Savelli et al.\textsuperscript{48} reported the structural and kinetic studies with new gemini surfactants \([\text{CH}_3-(\text{CH}_2)_m-\text{Me}_2N'\text{CH}_2\text{ArCH}_2N'\text{Me}_2-(\text{CH}_2)_m-\text{CH}_3]2\text{Br}^-\), where \(\text{CH}_3\text{ArCH}_2\) is the spacer, with \(\text{Ar} = 2,5-(\text{MeO})-\text{C}_6\text{H}_2\), with bromide as counterion and with \(m = 11, 13\) and \(15\), \(\text{pXMo(DDA)}_2\), \(\text{pXMo(MDA)}_2\), and \(\text{pXMo(CDA)}_2\), respectively. As kinetic probes they used decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion (6-NBIC) and hydrolysis of 2,4-dinitrophenyl phosphate dianion (2,4-DNPP2-) in presence of these new micellized surfactants.

Evidence of enhanced reactivity of 4-(Dialkylamino)pyridine (DAAP) based compounds toward dephosphorylation of hydrophobic tri-phenyl phosphate and deacylation of 4-nitrophenyl hexanoate esters reactions in cationic gemini micellar media was studied by Bhattacharya and Kumar\textsuperscript{28}.

Hydrolysis of \(p\)-nitrophenyl picolinate (PNPP) and \(p\)-nitrophenyl acetate (PNPA) mediated by the micellar catalytic systems of two types of cationic surfactants [cetyltrimethyl ammonium bromide (CTAB), Gemini dimethylene-1,2-bis(cetyltrimethyl ammonium bromide) (16-2-16, 2Br-)] were investigated by Xian-Jiang and coworkers\textsuperscript{49}. Similarly, Qin-Hui et al.\textsuperscript{50} investigated the hydrolysis of \(p\)-nitrophenyl picolinate (PNPP) mediated by the micellar catalytic systems of two gemini cationic surfactants with different hydrophobic tail groups (ethanediyl-1,2-bis(dodecyldimethylammonium bromide) (12-2-12, 2Br2), dimethylene-1,2-bis(cetyltrimethylammonium bromide) (16-2-16, 2Br2)) spectrophotometrically in the pH range of 7.0–9.0 and at 25 °C.

Recently, Chen et al.\textsuperscript{51} studied the cleavage of 2-hydroxypropyl \(p\)-nitrophenyl phosphate (HPPN) catalyzed by the Zn(II)-biap (biap: \(N,N\)-bis(2-ethyl-5-methylimidazole-4-ylmethyl) aminopropane) complex has been investigated spectrophotometrically in a micellar solution of cationic gemini surfactant 16-2-16
[bis (hexadecyldimethylammonium)ethane bromide] and CTAB (hexadecyltrimethylammonium bromide).

3.2 PRESENT INVESTIGATION

In the present study, we have extended our investigation to the nucleophilic substitution reaction of \( p \)-nitrophenyl acetate (PNPA) (I) and \( p \)-nitrophenyl diphenyl phosphate (PNPDPP) (II) with hydroxamate ions (III) in the presence of novel gemini surfactants.

\[
\begin{align*}
&\text{(I) } &\text{(II) } &\text{(III)} \\
&\begin{matrix}
\text{H}_2\text{C} & \text{C} & \text{O} & \text{aryl} & \text{NO}_2 \\
\end{matrix} & \begin{matrix}
\text{aryl} & \text{O} & \text{P} & \text{aryl} & \text{NO}_2 \\
\end{matrix}
\end{align*}
\]

- \( R = \text{CH}_3, \ R' = \text{H} \) (Acetohydroxamate ion, AHA)
- \( R = \text{C}_6\text{H}_5, \ R' = \text{H} \) (Benzohydroxamate ion, BHA)
- \( R = 2\text{-HOC}_6\text{H}_4, \ R' = \text{H} \) (Salicylhydroxamate ion, SHA)
- \( R = 2\text{-ClC}_6\text{H}_4, \ R' = \text{CH}_3 \) (\( N \)-Methyl-2-Chlorobenzohydroxamate ion, MCBHA)
- \( R = \text{C}_6\text{H}_5, \ R' = \text{C}_6\text{H}_5 \) (\( N \)-Phenylbenzohydroxamate ion, PBHA)

Depending upon reactant transfer and local rate constants, reaction may be accelerated by partitioning the reagents that can react in micellar interfacial region. Most papers on gemini surfactants have focused on their specific structural
properties, with few studies of their effects upon micellar catalysis \(^{48,54}\) and
cellular catalysis \(^{55}\). Moving along these lines, the hydrolysis of PNPA and
PNPDPP catalyzed by 16-n-16,2Br (IV) and 12py-n-py12,2Cl (V) gemini
surfactants were investigated.

\[
\begin{align*}
\text{CH}_3 & \quad \text{Br} & \quad \text{CH}_3 \\
\text{H}_3 & \quad \text{N} & \quad \text{N} - \text{CH}_3 \\
\text{C}_{16}\text{H}_{33} & & \text{C}_{16}\text{H}_{33} \\
\text{N} - \text{(CH}_2)_n & \quad \text{N} - \text{(CH}_2)_n \\
\text{C}_{12}\text{H}_{25} & & \text{C}_{12}\text{H}_{25}
\end{align*}
\]

16-3-16,2Br\(^{-}\) \((n = 3)\),
16-4-16,2Br\(^{-}\) \((n = 4)\),
16-6-16,2Br\(^{-}\) \((n = 6)\),
16-12-16,2Br\(^{-}\) \((n = 12)\)

(IV) \hspace{1cm} (V)

3.3 EXPERIMENTAL

3.3.1 Materials

\(N\)-Phenylbenzohydroxamic acid and benzohydroxamic acid were
prepared by the literature method \(^{56,57}\). \(N\)-methyl-2-chlorobenzohydroxamic acid
(MCBHA) was synthesized by the reaction of 2-chlorobenzoyl chloride and \(N\)-
methyl hydroxylamine hydrochloride. The ether solution of 2-chlorobenzoyl
chloride \((0.05\ \text{mol})\) and \(N\)-methyl hydroxylamine hydrochloride \((0.01\ \text{mol})\) was
stirred at room temperature in the presence of sodium carbonate \((0.01\ \text{mol})\).
Ether was evaporated and crude material was crystallized with dichloromethane
and hexane. The hydroxamic acid thus obtained was characterized by spectral
analysis. Salicylhydroxamic acid and acetoxyhydroxamic acid, were obtained from Sigma/Aldrich. PNPDP was prepared and purified by literature method. p-Nitrophenyl diphenyl phosphate was prepared at Defence Research Development Establishment, Gwalior by condensation of diphenyl chlorophosphate with p-nitrophenol in the presence of triethylamine.

All the samples of pyridinium gemini surfactants were the same reported in a previous paper. Ammonium Gemini surfactants were prepared according to well established protocols. Gemini surfactants were obtained from Dr. Pierluigi Quagliotto (Dipartimento di Chimica Generale ed Organica Applicata Università degli Studi di Torino, Italy).

3.3.2 Methods

All of the reactions were followed at 27 °C ± 0.2 °C with a UV 2-300 Unicam spectrophotometer equipped with Techne circulator (C-85A) thermostated cell holder, Cary 50 Varian UV-vis spectrophotometer and Systronics (104) spectrophotometer. The rate of nucleophilic reaction with PNPA and PNPDP were determined by following the increase in absorption of p-nitrophenoxide anion (400 nm). All of the kinetic experiments were performed at an ionic strength of 0.1 M (with KCl). Borate buffer was employed. All reactions were conducted under pseudo-first order conditions. For all of the kinetic runs, the result of absorbance/time fits very well to the first-order rate equation (3.1)

$$\ln (A_{\infty} - A_i) = \ln (A_{\infty} - A_0) - kt$$

The pseudo-first order rate constants can be determined by method of least squares. Each experiment was repeated at least twice, and the observed rate constant was
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found to be reproducible within a precision of about 3% or better. The spectrum exhibits an increase in absorbance at 400 nm with the formation of p-nitrophenoxide ion during the course of reaction. The pK_a values of hydroxamic acids were determined pH-meterically using Systronic (type-335) pH meter.

3.4 RESULTS AND DISCUSSION

3.4.1 Effect of pH

Pseudo-first order rate constants for the reaction of p-nitrophenyl acetate and p-nitrophenyl diphenyl phosphate with hydroxamate ions (Scheme 3.1) have been determined at 27 °C in the aqueous and acetonitrile (MeCN) media with the nucleophiles in large excess over the substrate.

![Scheme 3.1](image-url)

The pH-dependent rate constant increases with increasing value of pH in the range 6.7-11.0. The pH-rate constant profile shown in Figure 3.1 and data given
in Table 3.1 for the reaction of PNPDPP with N-methyl 2-chlorobenzohydroxamate and N-phenylbenzohydroxamate ions N-phenyl-benzohydroxamate ion in cationic micellar solution is typical of pH-dependent nucleophilic reaction.

Table 3.1
pH-Dependent pseudo-first order rate constants for the nucleophilic substitution reaction of p-nitrophenyl diphenyl phosphate with N-methyl 2-chlorobenzohydroxamate and N-phenylbenzohydroxamate ions in micellar solution at 27 °C.

<table>
<thead>
<tr>
<th>pH</th>
<th>MCBHA $k_{obs} \times 10^3$/s$^{-1}$</th>
<th>PBHA $k_{obs} \times 10^3$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.6</td>
<td>0.58</td>
<td>0.61</td>
</tr>
<tr>
<td>7.0</td>
<td>0.77</td>
<td>0.97</td>
</tr>
<tr>
<td>7.3</td>
<td>1.37</td>
<td>1.45</td>
</tr>
<tr>
<td>7.9</td>
<td>2.15</td>
<td>2.23</td>
</tr>
<tr>
<td>8.5</td>
<td>---</td>
<td>4.53</td>
</tr>
<tr>
<td>9.0</td>
<td>4.26</td>
<td>7.67</td>
</tr>
<tr>
<td>9.5</td>
<td>5.6</td>
<td>9.00</td>
</tr>
<tr>
<td>10.0</td>
<td>6.04</td>
<td>9.87</td>
</tr>
<tr>
<td>11.0</td>
<td>6.25</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Conditions: $\mu = 0.1$ M KCl, [PNPDPP] = 1.0 x $10^{-4}$ M, [MCBHA] = 1.0 x $10^{-3}$ M, [C$_{12}$-4-C$_{12}$, 2Cl] = 1.0 x $10^{-3}$ M, Medium 4 % MeCN.

The rate of reaction shows drastic change at the pH where the 50% hydroxamic acid deprotonated, i.e., pH*, of hydroxamic acid. The apparent pH* of all of the hydroxamic acids were determined in the presence of 12py-4-py, 12,2Cl$^-$.
The effect of cationic gemini surfactants on $pK_a$ is not much significant. The $pK_a$ value, thus, determined under micellar conditions agrees with the value determined pH-metrically. The pH-rate profile for the reaction of PNPDP with $N$-methyl-2-chlorobenzohydroxamate and $N$-phenylbenzohydroxamate ion in cationic gemini micellar solution is typical of a pH-dependent nucleophilic reaction. Hydroxamic acids have been suggested to behave either as NH or OH acids depending on solvents. Numerous studies indicate that hydroxamic acids are OH, rather than NH, acids in $H_2O$. It is known that the anion of hydroxamic acid (N-O) acts as a reactive species in the hydrolysis of esters. Consequently, the $pK_a$ for the conversion of the N-OH to N-O$^-$ form play an important role in the cleavage of phosphate esters. A pH-rate constant profile for the nucleophilic cleavage of

![pH-rate profiles for the reaction of PNPDP with N-methyl-2-chlorobenzohydroxamate and N-phenylbenzohydroxamate ions in cationic gemini micellar media.](image)
1.0 x 10⁻⁴ M PNPDP by 1.0 x 10⁻¹ M hydroxamate ions in 12py-4-py12,2Cl micellar media (1.6 x 10⁻³ M) gave the apparent pKₐ values for each of the hydroxamic acids. Typically, the pseudo-first order rate constants for the reaction of PNPDP were determined at different pH values between 6.7 and 11.0. In Figure 3.2, a representative pH-rate constant profile for the cleavage of 1.0 x 10⁻⁴ M PNPDP by 1.0 x 10⁻³ M of N-phenylbenzohydroxamate ions in micellar 12py-4-py12, 2Cl⁻ (1.6 x 10⁻³ M) at 27°C is shown.

![Figure 3.2: Plot of log k_{obs.} vs. pH for the reaction of PNPDP with N-phenylbenzohydroxamate (•) ions in cationic gemini Surfactant (12py-4-py12,2Cl).](image)

The plot of log k_{obs.} vs. pH (Figure 3.2) gave a break at pH 8.9 which was taken as a systematic apparent pKₐ for the PBHA under 12py-4-py12,2Cl micellar condition.
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Table 3.2

Kinetic parameters for the hydrolysis of PNPA in 12py-4-py12, 2Cl gemini surfactant micelles; [Surfactant]=5.0x10^{-3} M.

<table>
<thead>
<tr>
<th>Hydroxamate ion</th>
<th>pK_a</th>
<th>k_{obs} 10^3/s</th>
<th>*k_{rel}</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td></td>
<td>0.24</td>
<td>6</td>
</tr>
<tr>
<td>AHA</td>
<td>9.2</td>
<td>5.75</td>
<td>143</td>
</tr>
<tr>
<td>BHA</td>
<td>8.6</td>
<td>39.0</td>
<td>975</td>
</tr>
<tr>
<td>MCBHA</td>
<td>7.6</td>
<td>40.3</td>
<td>1007</td>
</tr>
<tr>
<td>PBHA</td>
<td>8.9</td>
<td>63.6</td>
<td>1590</td>
</tr>
</tbody>
</table>

Conditions: 0.06 M phosphate buffer, pH = 7.9, \( \mu = 0.1 \) M KCl, [PNPA] = 1.0 x 10^{-4} M, [HA] = 1.0 x 10^{-3} M, \( k_{obs}^0 = 0.04 \times 10^{-3} \) s^{-1}, \*k_{rel} = k_{obs}/k_{obs}^0. (\( k_{obs}^0 \) is the value of hydrolytic background reaction in buffer condition).

3.4.2 Effect of Nucleophile Concentration

To investigate the nucleophilic catalysis of hydroxamate ions for the decomposition of organophosphate, we have studied the reaction of PNPDPDPP in the presence and absence of hydroxamate ions. By comparing the observed pseudo-first-order rate constant in the presence of hydroxamic acids (\( k_{obs} \)) and in buffer alone (\( k_{obs}^0 \)), it is apparent that the addition of hydroxamic acids under these conditions increases the rate of nucleophilic reaction of PNPDPDPP significantly. The nucleophile concentration dependent first-order rate constant was determined for the reaction of PNPDPDPP with hydroxamic acids in excess (Fig.3.3). Kinetic data show additional support for the hypothesis that hydroxamic acid is acting as a nucleophilic catalyst for the reaction of PNPDPDPP (Table 3.3). Equation 3.2
describes the reaction of PNPDPP with nucleophiles, and $k_0$ defined in equation 3.3 corresponds to the intercept in the $k_{\text{obs}}$ vs $[\text{Nu}]$ plot. The term $k_{H_2O}$ may assume some significance for very weak nucleophiles and at very low $OH^-$ concentrations. At high pH, the intercept is dominated by the $k_{OH^-}$ term.

$$k_{\text{obs}} = k_0^{\text{obs}} + k_{Na}[\text{Nu}]$$

$$k_0^{\text{obs}} = k_{H_2O} + k_{OH^-}[OH^-]$$

Plotting $k_{\text{obs}}$ vs $[\text{Nu}]$ gave a straight line (Figure 3.3) with intercept $k_0^{\text{obs}}$. This indicates that competition with other nucleophiles, i.e., $OH^-$ and $H_2O$, is not expected and hydroxamate ions are very strong nucleophiles for the nucleophilic attack at the $P$ center of PNPDPP and $k_{\text{obs}}$ is simply given by $k_{\text{obs}} = k_{\text{Nu}}[\text{Nu}]$.

Table 3.3

Nucleophile concentration dependent pseudo-first order rate constants for the reaction of $p$-nitrophenyl diphenyl phosphate with $N$-methyl 2-chlorobenzohydroxamate ion in micellar solution at 27 $^\circ$C.

<table>
<thead>
<tr>
<th>[MCBHA] mM</th>
<th>$k_{\text{obs}} 10^3$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.34</td>
</tr>
<tr>
<td>0.5</td>
<td>1.69</td>
</tr>
<tr>
<td>1.0</td>
<td>4.24</td>
</tr>
<tr>
<td>1.5</td>
<td>5.32</td>
</tr>
<tr>
<td>2.0</td>
<td>6.55</td>
</tr>
</tbody>
</table>

Conditions: $pH = 9.1$, 0.06 M borate Buffer, $\mu = 0.1$ M KCl, [PNPDPP] = $1.0 \times 10^{-4}$ M, [C$_{12}$-4-C$_{12}$2Cl$^-]$ = $1.6 \times 10^{-3}$ M, Medium 4 % (v/v) MeCN.
3.4.3 Reaction of PNPA in Gemini Surfactants

The values of $k_{\text{obs}}$ for the nucleophilic reaction of PNPA with hydroxamate ions in 16-n-16, 2Br⁻ and 12py-n-12py, 2Cl⁻ are summarized in Table 3.5. To simplify the kinetic interpretation, surfactant concentrations were well above those of monomeric surfactant. For pyridinium surfactants, the concentration range extends also in the premicellar region. It is then easy to compare the rate constants- $k_{\text{obs}}$ (micelle) and $k_{\text{obs}}$ (aqueous) in micelle and water, respectively. Kinetic rate data reveals that rate of reaction increases with increasing surfactant concentration up to a certain concentration of gemini surfactants and then decreases. The pyridinium-based surfactant is more reactive than ammonium based cationic gemini surfactant. Table 3.4 reveals the kinetic rate data for the reaction of $p$-nitrophenyl acetate with hydroxamate ions in gemini surfactant at pH 8.0 and
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27 °C. It is evident from the kinetic data and rate profiles that micellar rate of the reaction increases with increasing length of spacer between dicationic head group of the dimeric surfactants. The value of $k_{\text{obs}}$ for the hydrolysis of PNPA by all the hydroxamate ions at $[12\text{py}-4\cdot12\text{py}, 2\text{Cl}] = 5.0 \times 10^{-1} \text{ M}$, is given in Table 3.5. The $k_{\text{rel}}$ shows the ratio of the hydrolytic rate constant of individual hydroxamate ions against the PNPA ($k_{\text{obs}}$) compared to the background hydrolytic rates in the buffered aqueous media in the absence of hydroxamate ions and gemini surfactants ($k_{\text{obs}}^0$). $N$-Substituted hydroxamate ions show large rate enhancement as compared to unsubstituted hydroxamate ions in the micellar condition. $N$-phenylbenzohydroxamate ion shows 1590-fold rate acceleration effect for the catalytic cleavage of PNPA.

3.4.4 Effect of Head group, Chain length and Spacer length

The rate effects in colloidal assemblies are sensitive to the length of hydrocarbon tail, the nature of cationic head group, counterion, the charge type of the amphiphile, and the head group bulk, giving information about structural variation of the submicroscopic reaction environments. It is generally observed that the micellar systems containing large chain length (tail) shows large $k_{\text{obs}}$ values than the micelle of smaller hydrocarbon tail because of the large aggregation of the long tailed surfactants. Surprisingly, the pyridinium-based gemini surfactant, 12py-n-py12,2Cl, showed large rate acceleration effects for the reaction of PNPA, in comparison to ammonium-based surfactants, 16-n-16,2Br, with longer hydrocarbon chain (tail). Changes in the partitioning of the reactants between water and micelles due to changes in substrate hydrophobicity, or the presence of competing ions, markedly affect overall rate constants and the rate-surfactant profiles, which can be fitted quantitatively in terms of distribution models. This
could come out from the ability that aromatic compounds have to stack in between the pyridinium rings nearly at the micellar surface.

Table 3.4
Summary of kinetic rate data for the reaction of p-Nitrophenyl acetate with hydroxamate ions in gemini surfactant at pH 8.0 and 27 °C.

<table>
<thead>
<tr>
<th>[Gemini] mM</th>
<th>[16-12-16, 2Br⁻]</th>
<th>[12py-4-12py, 2Cl⁻]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BHA</td>
<td>AHA</td>
</tr>
<tr>
<td>0</td>
<td>5.40</td>
<td>1.87</td>
</tr>
<tr>
<td>0.53</td>
<td>8.82</td>
<td>3.29</td>
</tr>
<tr>
<td>0.75</td>
<td>9.10</td>
<td>4.00</td>
</tr>
<tr>
<td>1.00</td>
<td>9.50</td>
<td>5.04</td>
</tr>
<tr>
<td>1.60</td>
<td>12.7</td>
<td>5.40</td>
</tr>
<tr>
<td>3.75</td>
<td>20.5</td>
<td>37.7</td>
</tr>
<tr>
<td>5.00</td>
<td>27.0</td>
<td>39.0</td>
</tr>
<tr>
<td>7.14</td>
<td>24.8</td>
<td>36.8</td>
</tr>
</tbody>
</table>

Conditions: 0.06 M phosphate buffer, pH = 7.9, [PNPA] = 1.0 x 10⁻⁴ M, [HA] = 1.0 x 10⁻³ M, μ = 0.1 M KCl, reaction medium = 5.33 % (v/v) MeCN.
It was also found that among the gemini surfactants as host micelles, the reactivity of the hydroxamate ions also depend on the gemini spacer chain length. Table 3.5 summarizes the influence of spacer length variation (n-values) on the esterolytic rate of PNPA by benzohydroxamate ion under comparable reaction conditions. It is interesting to note that the reactions in 16-n-16 geminis (16-3-16 to 16-12-16), gives observed maximum of \( k_{obs} \) at different surfactant concentrations. For example, gemini with spacer length 3-6 shows rate maximum at identical concentration i.e. 3.75 \( \times \) 10^{-3} M, whereas in 16-12-16,2Br gemini, the maximum rate have been observed at the surfactant concentration of 5.0 \( \times \) 10^{-3} M. The result data (Table 3.5) reveals that the values of \( k_{obs} \) shows ~3.5-fold acceleration effect with varying spacer length from 3 to 12. On the other hand, 12py-n-py12, 2Cl gemicelles shows rate maximum at identical concentrations and shows no significant effect with changing spacer length from 3 to 4. Although variation of spacer chain lengths alters the shape, critical micelle concentrations etc. of gemini micellar aggregates\(^{49-61}\), these changes do not appear to influence drastically the observed maximum of the rate constants for the ester cleavage reactions\(^{27}\). Borse et al.\(^{11}\) investigated the micellization behaviour of cationic gemini surfactants with varying head group, spacer lengths and tail groups. It has been well reported that the aggregation numbers (\( N \)) and dimension of micelle decreases when spacer chain length increases from 4 to 6, whereas very small change was observed in aggregation number and dimension of micelles when spacer chain length increased from 6 to 10. This can be attributed to the conformational changes of spacer at the micelle-water interface. The spacer remains mainly in extended conformation until it reaches the length of six methylenes, whereas for spacer length greater than 6 methylene units, it tries to form a loop extended toward the hydrophobic core of the micelles, disrupting the geometry of micelles.
Table 3.5

Summary of kinetic rate data for the reaction of p-nitrophenyl acetate with benzohydroxamate ions in Gemini surfactant with varying spacer length at pH 7.9 and 27°C. The concentrations are given in parenthesis from Reference 20.23.

<table>
<thead>
<tr>
<th>(k_{obs} \times 10^3 ) M⁻¹ s⁻¹</th>
<th>( [\text{Gemini} ] 16-n-16,2Br )</th>
<th>( [\text{Gemini} ] 12-py-n-py )</th>
<th>( [\text{Gemini} ] 12-py-12Cl )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n = 3 )</td>
<td>( n = 4 )</td>
<td>( n = 6 )</td>
<td>( n = 12 )</td>
</tr>
<tr>
<td>3.8</td>
<td>3.2</td>
<td>3.8</td>
<td>2.4</td>
</tr>
<tr>
<td>3.9</td>
<td>3.8</td>
<td>3.0</td>
<td>2.7</td>
</tr>
<tr>
<td>3.7</td>
<td>3.1</td>
<td>0.0</td>
<td>2.0</td>
</tr>
<tr>
<td>3.6</td>
<td>1.7</td>
<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td>1.2</td>
<td>1.1</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>1.9</td>
<td>1.0</td>
<td>0.8</td>
<td>0.62</td>
</tr>
<tr>
<td>1.6</td>
<td>1.0</td>
<td>0.75</td>
<td>0.62</td>
</tr>
<tr>
<td>0.8</td>
<td>0.75</td>
<td>0.62</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Conditions: 0.06 M phosphate buffer, pH 7.9, \( [\text{KCl}] = 0.1 \) M, \( [\text{PNPA}] = 1.0 \times 10^{-4} \) M, \( [\text{BHA}] = 1.0 \times 10^{-3} \) M. The concentrations are given in parenthesis from Reference 20.23. In 20% (v/v) MeCN-H₂O medium.
It may therefore be concluded that, amongst all gemini surfactants, 16-12-16,2Br and 12py-4-12py,2Cl, dicationic surfactants are better catalyst for the hydrolytic reaction of PNPA, probably because the spacer decreases the extent of water penetration at the aggregate surface. The nucleophilic reaction of PNPA and PNPDPp are assisted by a decrease in the water content of the reaction environment. Menger et al.\textsuperscript{62} have used chemical trapping to estimate concentration of H\textsubscript{2}O and Br\textsuperscript{-} at surface of gemini micelles and concluded that proximity of the positive charges increases the anion binding at the expense of binding of H\textsubscript{2}O, which provides a ready explanation of our kinetic data. This is further supported by the observation that the degree of counterion binding increases for short spacer gemini surfactants with respect to their corresponding "monomers" (CTAB) for the 16-n-16,2Br\textsuperscript{-} and dodecylpyridinium chloride for the 12py-4-12py,2Cl\textsuperscript{-}.\textsuperscript{68}

However, the change of length of spacer has little effects on $k_{obs}$, although it has major effects on solubility of ammonium gemini surfactants.\textsuperscript{63}

3.4.5 Catalytic Cleavage of PNPDPp in Gemini Micelles

When solublized in pH 9.1 micellar 16-12-16,2Br\textsuperscript{-} and 12py-4-py12,2Cl\textsuperscript{-}, hydroxamate ions act as an efficient catalyst for the cleavage of $p$-nitrophenyl diphenyl phosphate (PNPDPp). The actual source of catalytic power is $\alpha$-nucleophilicity of hydroxamate ion, which appears to be powerful $O$-nucleophile. The deprotonated form of hydroxamic acid acts as effective nucleophiles with the hydrolytic reaction for the organophosphorus compounds proceeding via a step outlined in Scheme 3.2.
Figure 3.4: Plots of $k_{obs}$ for the hydrolysis of PNPA ($1.0 \times 10^{-4}$ M) by BHA ($1.0 \times 10^{-3}$ M) vs. different host surfactant concentrations in pH 7.9, 0.06 M phosphate buffer at 27°C as a function of (A) $\{[16-(CH)_{n-16,2Br}]$ where $n = 3, 4, 6, 12\}$ (B) $\{[12py-n-12py,2Cl]\}$ gemini surfactants. Lines are drawn to show the trend.
Table 3.6 summarizes the \( k_{\text{obs}} \) values for the nucleophilic reaction of PNPDPD with hydroxamate ions in aqueous and gemini micellar media. The catalysis of the cleavage of PNPDPD (1.0 \( \times 10^{-4} \) M) by hydroxamate ion is accelerated by the factor \( \sim 4.0 \) to 10-fold in the absence of micellar aggregate, since the value of \( k^0_{\text{obs}} \) for the background reaction of PNPDPD in the buffered condition is 0.03 \( \times 10^{-3} \) s\(^{-1}\). The \( k^0_{\text{obs}} \) value for the hydrolytic background reaction is quite in agreement with the rate 0.0291 \( \times 10^{-3} \) at pH 9.0 reported by Moss and co-workers\(^{69}\).

From Table 3.4, it can be observed that 16-12-16,2Br\(^-\) and 12py-4-py12,2Cl\(^-\) surfactant micelles showed different catalytic efficacy on the nucleophilic cleavage of PNPDPD by the different hydroxamate ions. The 16-12-16,2Br\(^-\) micelle showed 73-fold catalysis with \( N \)-phenylbenzohydroxamate ion (1.0 \( \times 10^{-3} \) M). Under the identical concentration of 12py-4-py12,2Cl\(^-\) micelle showed 255-fold rate enhancement. It is also interesting to note that the pyridinum-based gemini is 3-fold more reactive than ammonium-based gemini surfactant.
Table 3.6
Rate constants ($k_{ob}$, s$^{-1}$) for the hydrolysis of PNPDPP catalyzed by various hydroxamate ions in gemini Micelles$^a$.

<table>
<thead>
<tr>
<th>[Gemini]</th>
<th>(16-12-16,2Br^-)</th>
<th>(12py-4-py12,2Cl^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mM</td>
<td>BHA</td>
<td>PBHA</td>
</tr>
<tr>
<td>0</td>
<td>0.15</td>
<td>0.13</td>
</tr>
<tr>
<td>0.53</td>
<td>….</td>
<td>1.74</td>
</tr>
<tr>
<td>0.75</td>
<td>….</td>
<td>….</td>
</tr>
<tr>
<td>1.00</td>
<td>0.79</td>
<td>1.90</td>
</tr>
<tr>
<td>1.60</td>
<td>0.87</td>
<td>2.19</td>
</tr>
<tr>
<td>3.74</td>
<td>0.64</td>
<td>1.87</td>
</tr>
<tr>
<td>5.00</td>
<td>0.60</td>
<td>1.58</td>
</tr>
</tbody>
</table>

$^a$Conditions: 0.06 M borate buffer, pH = 9.1, 27°C; [PNPDPP] = 1.0 x 10$^{-4}$ M, [HA] = 1.0 x 10$^{-3}$ M, Reaction medium 3.3 % (v/v) MeCN, $k_{ob}^0 = 0.030$ x 10$^{-3}$ s$^{-1}$ ($k_{ob}^0$ is the value of hydrolytic background reaction in buffer condition).

The enhanced rate for the nucleophilic reactions of anionic nucleophiles has often been observed in the cationic micellar media. Clearly, the rate enhancement is associated with the presence of micelles in the system and may be attributed to the so-called "concentration effect" in the micelle$^{69-71}$. The electrostatic attraction of the cationic head group of the surfactants at the micelle surface to the nucleophilic anion counterions leads to augmentation of the local concentration of the nucleophile, while incorporation of the substrate in the micelle leads to a higher local concentration of the reactants. This enhanced concentration of the reactants accounts for the higher rate of reaction. Implicit in this explanation
is the requirement that the reactive site of the PNP-DPP be situated in close proximity to the nucleophile, that is, at the micelle-water interface, in the Stern layer. The subsequent addition of the cationic gemini surfactant after $k_{\text{obs}}^\text{max}$ caused a decrease in the reaction rate, possibly due to the decrease in the catalyst/reagent concentration in the micellar pseudophase. The excess of unreactive counterions ($X'$) competes with hydroxamate ions for available sites in the Stern layer.

At this point it is appropriate to compare the reactivity of PBHA and MCBHA for the cleavage of PNP-DPP. The pK$_a$ value of the MCBHA is 7.65 and hence ionizes significantly as reactive hydroxamate ion as compared to the PBHA (pK$_a$ 8.9). Therefore, MCBHA must be more reactive than PBHA due to the electrostatic attraction into the cationic micelles. Surprisingly, PBHA shows larger rate acceleration effect due to the hydrophobic as well as electrostatic attraction into the micelles. We observed similar results for the nucleophilic dephosphorylation reaction of $p$-nitrophenyl diphenyl phosphate with many $N$-substituted and unsubstituted hydroxamate ions in cetylpyridinum bromide micelle. Such reactivity patterns have also been observed by Morales-Rojas and R. A. Moss while studying the nucleophilic reactivity of the iodosyl nucleophiles with varying hydrophobicity of the nucleophiles in CTA$^+$ micelle. The data in Table 3.6 reveals that the hydrophobicity of hydroxamate nucleophile greatly influences its reactivity.

3.4.6 Applications of the pseudophase model

Quantitative treatments of reactivity in association colloids frequently use the pseudophase model, which predict that values of $k_{\text{obs}}$ will increase (or decrease) monotonically and become constant with fully bound substrate. Reagents that are partitioned into the micelles can react in interfacial region, which is regarded as
a pseudophase distinct from bulk solvent. Depending upon the interaction of substrate into the micelle, rate of reaction is accelerated or inhibited. The influence of gemini micelle on the $k_{\text{obs}}$ values for the nucleophilic bimolecular reactions of PNPA and PNPDPN with hydroxamate ions can be described as illustrated in Scheme 3.3.

![Scheme 3.3](image)

In Scheme 3.3, subscripts $w$ and $m$ indicate aqueous and micellar pseudophases, respectively, and $D_n$ represents the micellized surfactant, that is, $[D_n] = [D]_{T\text{-cmc}}$, where $[D]_T$ is the stoichiometric surfactant concentration and cmc the critical micellar concentration, obtained under the experimental conditions as the minimum surfactant concentration required to observe any kinetic effect. The distribution constant of the HA throughout the 2 pseudophases is expressed by means of the following expression:

$$K_{HA}^{\text{diff}} = \frac{[HA]_m}{[HA]_w [D_n]} \quad 3.4$$

By means of a simple balance of matter we can obtain the following expressions for the HA concentration:
The distribution constant of the ESTER is:

$$K_{m}^{ESTER} = \frac{[ESTER]_{w}}{[ESTER]_{m}[D_n]}$$  \hspace{1cm} 3.4.2

By means of a simple balance of matter we can obtain:

$$[ESTER]_{m} = \frac{[ESTER]_{r}}{1 + K_{m}^{ESTER}[D_n]}$$

$$[ESTER]_{m} = \frac{[ESTER]_{r}K_{m}^{ESTER}[D_n]}{1 + K_{m}^{ESTER}[D_n]}$$  \hspace{1cm} 3.4.3

The rate equation is:

$$rate = k[ESTER]_{r}[HA]_{r}$$  \hspace{1cm} 3.4.4

$$rate = k_{obs}[ESTER]_{r}$$  \hspace{1cm} 3.4.5

Equation (4.4) can be rewritten as:

$$rate = rate_{wa} + rate_{wa}$$  \hspace{1cm} 3.4.6

The HA concentration in the micellar pseudophase has been defined as the local, molar concentration within the micellar pseudophase: $[HA]_{w} = \frac{[HA]_{m}}{V}$ where $V$ is the molar volume in $\text{dm}^3\text{mol}^{-1}$ of the reaction region and $[D_n]V$ denotes the
micellar fractional volume in which the reaction occurs. The HA concentration in the water pseudophase is $[HA]_w = [HA]_a$.

The expression for the observed rate constant, $k_{obs}$, based on the above considerations, is given by the following equation:

$$k_{obs} = k_2^w + \frac{k_2^m}{V} K_m^{'SCH} K_m^{HA} [D_n] [HA]^r$$

Scheme 3.3 considers the distribution of PNPA and PNPDPDPP between the aqueous and micellar pseudophases, $K_m^{PNPA}$ and $K_m^{PNPDPP}$. The association constants of PNPA and PNPDPDPP have been obtained from fitting the reaction data with the values of $K_m^{PNPA} = 185 \text{ M}^{-1}$ and $K_m^{PNPDPP} = 1200 \text{ M}^{-1}$ in 16-12-16,2Br$^-$ and $K_m^{PNPDPP} = 2500 \text{ M}^{-1}$ in 12py-4-py12,2Cl$^-$ gemini micelles. The distribution of the hydroxamate ion, HA, between both pseudophase is considered through the distribution constant $K_m^{HA}$. The different reactivities in the aqueous and micellar pseudophase have been taken into account through the corresponding second-order rate constants: $k_2^w$ and $k_2^m$. The values of $k_2^w$ have been obtained by studying the reaction in the absence of the surfactant. We assume $V$ equal to the partial molar volume of the interfacial reaction region in the micellar pseudophase, determined by Bunton$^{76}$ as 0.14 dm$^3$ mol$^{-1}$. Micellar binding of both substrate, PNPA and PNPDPDPP and hydroxamate ions HAs, is governed by hydrophobic interactions and the equilibrium constants $K_m^{PNPA}$, $K_m^{PNPDPP}$ and $K_m^{HA}$ are expressed by referring these concentrations to the total volume of the micelle.

The results presented in Table 3.7 allow us to study the influence of the nature of the micelle for the reaction of PNPA with unsubstituted and
Table 3.7

<table>
<thead>
<tr>
<th>Hydroxamate</th>
<th>$k_1^a$ ($M^{-1} s^{-1}$)</th>
<th>$K_{a}^{PNPP}$ ($M^{-1}$)</th>
<th>$K_{a}^{AP}$ ($M^{-1}$)</th>
<th>$k_{r1}^a$ ($M^{-1} s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHA</td>
<td>185</td>
<td>185</td>
<td>328</td>
<td>1.82 x 10^{-9} *10^{-4}</td>
</tr>
<tr>
<td>BHA</td>
<td>5.40</td>
<td>185</td>
<td>40</td>
<td>1.02 x 10^{-12} *10^{-4}</td>
</tr>
<tr>
<td></td>
<td>5.40</td>
<td>185</td>
<td>40</td>
<td>2.28 x 10^{-28} *10^{-4}</td>
</tr>
<tr>
<td>MCHBHA</td>
<td>2.18</td>
<td>185</td>
<td>28</td>
<td>4.46 x 10^{-50} *10^{-4}</td>
</tr>
<tr>
<td>PHA</td>
<td>3.68</td>
<td>185</td>
<td>138</td>
<td>2.13 x 10^{-10} *10^{-4}</td>
</tr>
</tbody>
</table>

a. Kinetic parameters for the reactions in 16-12-16Br micelle

Conditions: 0.06 M phosphate buffer, pH = 7.9, $\mu = 0.1 M$ KCl

A substituted hydroxamate ion. From the fitting of equation 3.47, we obtained $k_1^a = 4.46 \times 10^{-1} M^{-1} s^{-1}$ and $2.13 \times 10^{-1} M^{-1} s^{-1}$ for the highly reactive gemini micellar systems (MCHBHA/12py-4-py12,2Cl and PHA/12py-4-py12,2Cl).

Likewise we obtained $k_{r1}^a = 3.02 \times 10^{-1} M^{-1} s^{-1}$, for the BHA/12py-4-py12,2Cl and $k_{r1}^a = 2.28 \times 10^{-2} M^{-1} s^{-1}$ for the BHA/16-12-16Br combination. On the basis of these results it can be concluded that the pyridinium-based micelles shows higher reactivity than the ammonium-based dimeric gemini micelles.

The analysis of the kinetic parameters of the micelle catalyzed reaction of PNPP can explain the reactivity pattern of the hydroxamate ions in both the gemini micellar media. Table 3.8 summarizes the values of $K_{a}^{PNPP}$, $K_{a}^{AP}$ and $k_{r1}^a$.
### Kinetic Parameters Obtained by Applying Pseudophase Model for the Nucleophilic Reaction of PNPDPP with Hydroxamate Ions in the Presence of 12py-4-py12,2Cl- and 16-12-16,2Br- Micelles

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>[H+] (M)</th>
<th>Determined pH</th>
<th>[PNPDPP] (M)</th>
<th>k1 (X 10^4 M^-1) s^-1</th>
<th>k2 (X 10^-2 M^-1) s^-1</th>
<th>Standard Error of Determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHA</td>
<td>0.13</td>
<td>16-12-16,2Br-</td>
<td>0.15</td>
<td>7.28 ± 0.70 X 10^-4</td>
<td>0.13</td>
<td>370</td>
</tr>
<tr>
<td>PBHA</td>
<td>0.15</td>
<td>12py-4-py12,2Cl</td>
<td>0.13</td>
<td>2.16 ± 0.17 X 10^-3</td>
<td>0.15</td>
<td>75</td>
</tr>
<tr>
<td>MCBHA</td>
<td>0.34</td>
<td>12py-4-py12,2Cl</td>
<td>0.34</td>
<td>1.15 ± 0.34 X 10^-2</td>
<td>0.15</td>
<td>70</td>
</tr>
<tr>
<td>PBHA</td>
<td>0.13</td>
<td>12py-4-py12,2Cl</td>
<td>0.13</td>
<td>1.79 ± 0.50 X 10^-2</td>
<td>0.15</td>
<td>85</td>
</tr>
<tr>
<td>PBHA</td>
<td>0.19</td>
<td>12py-4-py12,2Cl</td>
<td>0.19</td>
<td>3.04 ± 0.56 X 10^-3</td>
<td>0.15</td>
<td>75</td>
</tr>
</tbody>
</table>

Conditions: 0.06 M borate buffer, pH = 9.1, 27°C, [KCl] = 0.1 M KCl.

Table 3.8
for the reaction of PNPDP. Simulated rate surfactant profiles for PNPDP are shown in Figs.3.5 and 3.6. It can be seen from the plots that the agreement between the experimental and theoretical kinetic data was fairly good.

The results presented in Table 3.5 and Figures 3.5 and 3.6, also support the observation that the gemini surfactant with pyridinium head group is more reactive than gemini with ammonium head group. Further support for the differential reactivity can be obtained from the comparison of the values of $k_2^n$ at the micellar interface. The 12Py4-py12,2Cl micelle shows ~8-fold and ~4-fold catalytic advantage than 16-12-16,2Br micelles for the reaction of PNPDP with PBHA and BHA, respectively. An alternative explanation can be given with assumption: (a) large incorporation of PNPDP in the gemini surfactant of pyridinium head group (b) Effective nucleophilicity of PBHA in the presence of gemini surfactant (c) readily exchangeability of the Cl$^-$ counter ion than Br$^-$. The large value for association constant of PNPDP in gemini pyridinium micelles can be supported by the ability of aromatic rings to stack on pyridinium rings. Orientation of PNPDP in pyridinium gemini surfactant-hydroxamate can be described by the model presented by Balakrishnan et al. for the case of nonomeric cationic surfactant system. This can give specific interactions, leading to better packing of the solute into the pyridinium micelles than into the ammonium micelles. In general the nucleophilicity is strengthened by a less polar medium. A micellar medium can host reagents in a location having the polarity of alcohols (e.g. methanol, ethanol, etc.) or a bit less. The binding of Br$^-$ counterions to the pyridinium micelles (and in general cationic micelles) is tighter than that of Cl$^-$ counterions. The nucleophiles studied here can interact with cationic micelles by both charge and hydrophobic interactions. It is well known that aromatic counterions can induce pyridinium surfactants to give viscoelastic solutions and
Figure 3.5: Simulated rate-surfactant profiles for the reaction of \( p \)-nitrophenyl diphenyl phosphate with benzohydroxamate and \( N \)-phenylbenzohydroxamate ions in 16-12-16.2Br\(^-\) gemini surfactant (lines are predicted values with model).

Figure 3.6: Simulated rate-surfactant profiles for the reaction of \( p \)-nitrophenyl diphenyl phosphate with hydroxamate ions in 12Py-4-py12,2Cl\(^-\) gemini surfactant (lines are predicted values with model).
strong degree of counterion binding. The combination of the two interactions can lead to a high binding of the hydroxamate ions, thus exchanging with the chlorides.

The nucleophilic reactions in micelles are generally governed by basicity and the incorporation of different nucleophiles into the micelle (Figure 3.7).

![Chemical Structure](image)

**Figure 3.7**: Depiction of \( p \)-nitrophenyl diphenyl phosphate and hydroxamate orientations at micellar interface of 12py-n-py12,2Cl gemini micelle.

### 3.5 CONCLUSION

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. Herein kinetic studies have been performed for the hydrolysis of $p$-nitrophenyl acetate and $p$-nitrophenyl diphenyl phosphate using $\alpha$-nucleophile hydroxamate ions in the presence of gemini surfactants with quaternary ammonium bromide and pyridinium chloride head groups. Pyridinium gemini surfactants show higher reactivity than trimethylammonium ones. The arrangement of different head groups at micellar surface can leave different space for the reactant in order to attach (first) and enter (in a second time) the micelle. The phenyl ring of the reactant can stack between the pyridinium ring due to both electrostatic interactions and probable steric head group requirements at the micellar surface. This could give those micelles the possibility to better accommodate the reactant.

This work presents a new set of results on a well studied reaction in the presence of novel gemini surfactants. There is great potential for the use of $\alpha$-nucleophile-gemini surfactant medium for the detoxification of toxic organophosphorus compounds. More work is needed, however, to get a deeper insight on the role of novel gemini pyridinium surfactants for the detoxification of toxic organophosphates and pesticides.
REFERENCES


Effect of Cationic Gemini Surfactants on hydrosylation using Hydrazine

14 X. Han, V. K. Balakrishnan, G. W. VanLoon and E. Bunce, Langmuir, 2006, 22, 9009.
Effect of Cationic Gemini Surfactants on hydrolysis using Hydroxamate ion


Effect of Cationic Gemini Surfactants on hydrolysis using Hydroxamate ion


