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ORIGINAL CONTRIBUTION

Effect of cationic gemini surfactants on the hydrolysis of carboxylate and phosphate esters using hydroxamate ions

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Abstract 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$^-$, *n*=3, 4, 6, 12) and pyridinium chloride (12py-*n*-py12,2Cl$^-$, *n*=3, 4) head group have been investigated at 27 °C. The gemini surfactant with the pyridinium head group, 12-py-4-py12,2Cl$^-$ (tetramethylene-1,4 *bis* dodecylpyridinium chloride) shows a large rate acceleration effect than that with an 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. Catalytic system *N*-phenylbenzohydroxamate/12py-4-py12,2Cl$^-$ demonstrated over ~1,590-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.

Keywords Gemini surfactant · Phosphate and Carboxylate esters · Hydroxamate ions · Hydrolysis

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Introduction

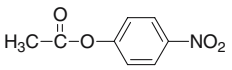
Gemini surfactants are composed of two monomeric surfactant molecules connected by a spacer chain [1]. They constitute a new class of amphiphilic molecules having its own distinct behavior [1, 2]. Since their first systematic studies over a decade ago, gemini surfactants have been the subject of intensive 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 [3–7].

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 [8–11]. Recently, Borse et al.[11] investigated the aggregation behavior of some novel class of gemini surfactants containing monoethanol and diethanol, e.g., 12-*4*-12 dodecanoyl monoethanol amide and 12-*4*-12 diethanol amine, head groups. As 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.

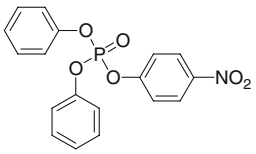
Current interest in studying the reactions of α-nucleophiles has received major importance in many applications of this highly reactive species [12–26]. For example, in the development of protocols for environmental decom-

position of sites polluted with organophosphorus insecticides, α-nucleophiles such as oximates [12–15], hydroxamates [16–18], hydroperoxide [19–21], iodosobenzoate [22–24], and hydroxybenzotriazoles [25] and tetrazole [26], etc., has been demonstrated to be highly effective. The need to develop efficient means to destroy stickpiles of organophosphorus nerve agents have led a number of groups to investigate different approaches toward enhancing decomposition of these agents [12–26]; α-nucleophiles can accelerate these decomposition. In this regard, we have been studying the esterolytic cleavage of carboxylate and phosphate esters using hydroxamate ions in cationic micellar media [32–36].

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.



(I)

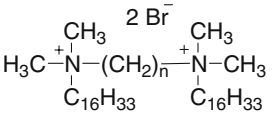


(II)

(III)

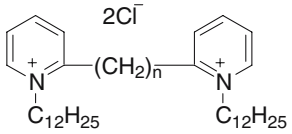
R = CH_3, R' = H (acetohydroxamate ion, AHA)
R = C_6H_5, R' = H (benzohydroxamate ion, BHA)
R = 2-HOC_6H_4, R' = H (salicylhydroxamate ion, SHA)
R = 2-ClC_6H_4, R' = CH_3 (*N*-methyl-2-Chlorobenzohydroxamate ion, MCBHA)
R = C_6H_5, R' = C_6H_5 (*N*-phenylbenzohydroxamate ion, PBHA)

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 [27–40] and metallomicellar catalysis [41]. 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.



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)



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

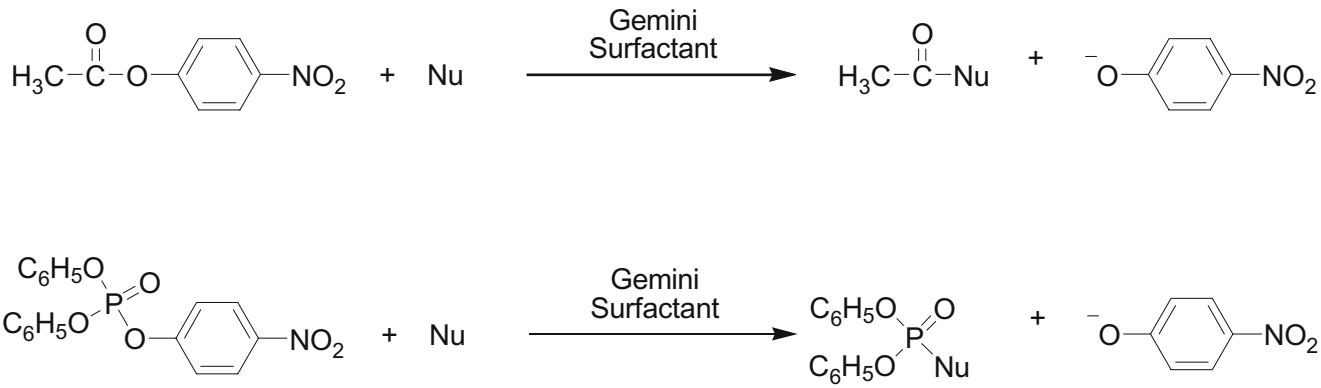
(V)

Results and discussion

Effect of pH

Pseudo-first-order rate constants for the reaction of PNPA and PNPDPP with hydroxamate ions (Scheme 1) have been determined at 27 °C in the aqueous and acetonitrile (MeCN) media with the nucleophiles in large excess over the substrate. The pH-dependent rate constant increases with increasing value of pH in the range 6.7–11.0.

The rate of reaction shows drastic change at the pH where the 50% hydroxamic acid deprotonated, i.e., pK_a, of hydroxamic acid. The apparent pK_a of all of the hydroxamic acids were determined in the presence of 12py-4-py12,2Cl^- (Table 1). 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 meterically. The pH rate profile for the reaction of PNPDPP with *N*-methyl-2-chlorobenzohydroxamate and *N*-phenylbenzohydroxamate ion in cationic gemini micellar solution is typical of a pH-dependent nucleophilic



Scheme 1 Reaction of PNPA and PNPDPP with hydroxamate ions

Table 1 Kinetic parameters for the hydrolysis of PNPA in 12py-4-py12.2Cl$^-$ gemini surfactant micelles [Surf]=5.0×10^{-3} M

Hydroxamate ion	pK_a	$k_{obs}\times10^3$ (s^{-1})	[a]k_{rel}
None		0.24	6
AHA	9.2	5.75	143
BHA	8.6	39.0	975
MCBHA	7.6	40.3	1007
PBHA	8.9	63.6	1590

Conditions: 0.06 M phosphate buffer, pH=7.9, μ=0.1 M KCl, [PNPA]=1.0×10^{-4} M, [HA$^-$]=1.0×10^{-3} M,k^0_{obs}=0.04×10^{-3} s^{-1} ($k^0_{obs}$is the value of hydrolytic background reaction in buffer condition) a$k_{rel} = k_{obs}/k^0_{obs}$

reaction. Hydroxamic acids have been suggested to behave either as NH or OH acids depending on solvents [42–45]. Numerous studies indicate that hydroxamic acids are OH, rather than NH, acids in H_2O [42, 43]. 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 1.0×10^{-4} M PNPDPP by 1.0×10^{-3} M hydroxamate ions in 12py-4-py12,2Cl$^-$ micellar media (1.6×10^{-3} M) gave the apparent pK_a values for each of the hydroxamic acids. Typically, the pseudo-first-order rate constants for the reaction of PNPDPP were determined at different pH values between 6.7 and 11.0. In Fig. 1, a representative pH rate constant profile for the cleavage of 1.0×10^{-4} M PNPDPP by 1.0×10^{-3} M of *N*-phenylbenzohydroxamate ions in micellar 12py-4-py12,2Cl$^-$ (1.6×10^{-3} *M*) at 27 °C is shown. .

The plot of log k_{obs} vs pH (Fig. 1) gave a break at pH 8.9, which was taken as a systematic apparent pK_a for the *N*-phenylbenzohydroxamate (PBHA) under 12py-*4*-py12.2Cl$^-$ micellar condition.

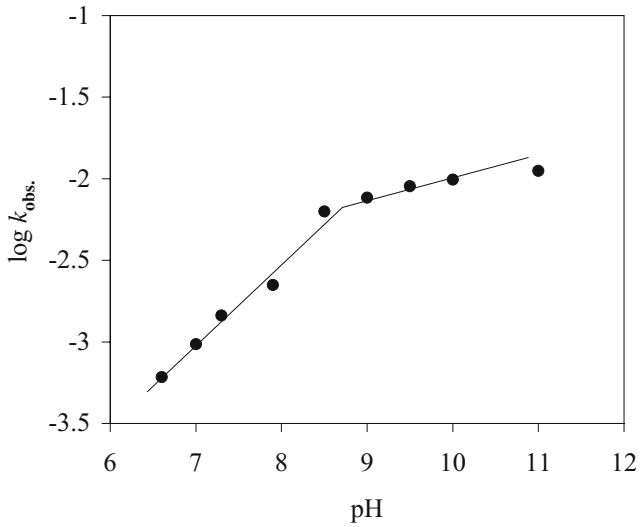


Fig. 1 Plot of log k_{obs} vs pH for the reaction of PNPDPP with *N*-phenylbenzohydroxamate (*filled circles*) ions in the cationic gemini surfactant (12py-*4*-py12,2Cl$^-$)

To investigate the nucleophilic catalysis of hydroxamate ions for the decomposition of organophosphate, we have studied the reaction of PNPDPP 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^0_{obs}), it is apparent that the addition of hydroxamic acids under these conditions increases the rate of nucleophilic reaction of PNPDPP significantly. The nucleophile concentration-dependent first-order rate constant was determined for the reaction of PNPDPP with hydroxamic acids in excess (Fig. 2). Kinetic data show additional support for the hypothesis that hydroxamic acid is acting as a nucleophilic catalyst for the reaction of PNPDPP. Equation 1 describes the reaction of PNPDPP with nucleophiles, and k^0_{obs} defined in Eq. 2 corresponds to the intercept in the k_{obs} vs [Nu] plot. The k_{H2O} term 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.

$$k_{obs} = k^0_{obs} + k_{Nu}[Nu] \quad (1)$$

$$k^0_{obs} = k_{H_2O} + k_{OH^-}[OH^-] \quad (2)$$

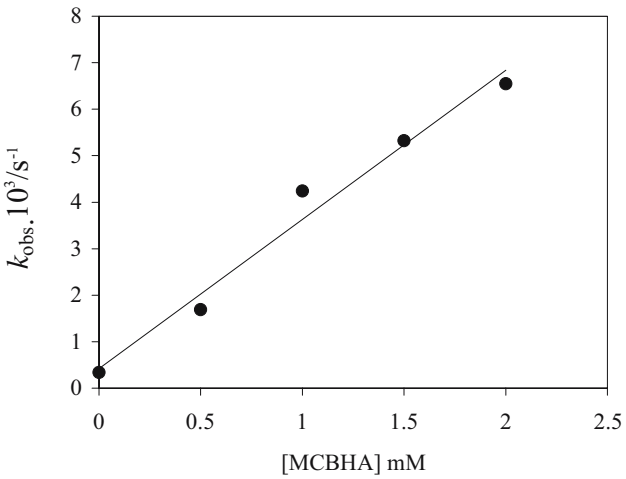


Fig. 2 Plot of $k_{obs}\times10^3$ (s^{-1}) vs concentration of *N*-methyl-2-chlorobenzo-hydroxamate ion in the 12py-4-py12,2Cl$^-$ micellar media, pH=7.9

Plotting k_{obs} vs [Nu] gave a straight line (Fig. 2) with intercept k^0_{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_{obs} is simply given by $k_{obs}=k_{Nu}[Nu]$.

Reaction of PNPA in gemini surfactants

The k_{obs} values for the nucleophilic reaction of PNPA with hydroxamate ions in 16-*n*-16.2Br^- and 12py-*n*-12py.2Cl^- are summarized in Table 2. To simplify the kinetic interpretation, surfactant concentrations were well above those of the monomeric surfactant. For pyridinum surfactants, the concentration range extends also in the premicellar region. It is then easy to compare rate constants, k_{obs} (micelle) and k_{obs} (aqueous) in micelle and water, respectively. Kinetic rate data reveal 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 the ammonium-based cationic gemini surfactant. It is evident from the kinetic data and rate profiles that micellar rate of the reaction increases with increasing length of spacer between the dicationic head group of the dimeric surfactants. The values of k_{obs} for the hydrolysis of PNPA by all the hydroxamate ions at [12py-*4*-12py.2Cl^-]=5.0×10^{-3} M are given in Table 2. The k_{rel} shows the ratio of the hydrolytic rate constant of individual hydroxamate ions against the PNPA (k_{obs}) compared to the background hydrolytic rates in the buffered aqueous media in the absence of hydroxamate ions and gemini surfactants (k^0_{obs}). *N*-Substituted hydroxamate ions show large rate enhancement as compared to unsubstituted hydroxamate ions in the micellar condition. The *N*-Phenylbenzohydroxamate ion shows 1,590-fold rate acceleration effect for the catalytic cleavage of PNPA.

Effect of head group, chain length and spacer length

The rate effects in colloidal assemblies are sensitive to the length of the hydrocarbon tail, the nature of cationic head group, the 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 a large chain length (tail) shows large k_{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 a longer hydrocarbon chain (tail). Changes in the partitioning of the reactants between water and micelles because of 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 pyridinium rings nearly at the micellar surface.

We 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 2 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

Table 2 Summary of kinetic rate data for the reaction of *p*-nitrophenyl acetate with benzohydroxamate ions in the gemini surfactant with varying spacer length at pH 7.9 and 27 °C

[Gemini]×10^{-3} M	$k_{obs}\times10^3$ (s^{-1})					
	16-*n*-16,2Br^-				12py-*n*-py12,2Cl^-	
	n=3[a] (0.0255 mM)	*n*=4[a] (0.027 mM)	*n*=6[a] (0.043 mM)	*n*=12 (0.02 mM)	*n*=3 (1.51 mM)	*n*=4 (1.28 mM)
0	4.40	4.40	4.40	5.40	5.40	5.40
0.53	5.31	4.41	4.70	8.82	8.70	10.4
0.75	–	5.65	5.90	9.10	10.9	13.0
1.0	5.65	–	6.30	9.50	13.2	16.2
1.60	5.94	6.23	6.81	12.7	17.3	20.6
3.75	7.41	7.12	8.00	20.5	28.0	37.7
5.00	7.23	–	–	27.0	38.0	39.0
7.14	7.10	7.00	7.90	24.8	32.6	36.8

Conditions: 0.06 M phosphate buffer, pH 7.9, μ=0.1 M KCl, [PNPA]=1.0×10^{-4} M, [BHA]=1.0×10^{-3} M. The cmc values (taken from [20, 23]) are given in parenthesis.
[a] In 20% (v/v) MeCN–H_2O medium

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., 3.75×10^{-3} M, whereas in the 16-12-16,2Br$^-$ gemini, the maximum of the rate have been observed at the surfactant concentration of 5.0×10^{-3} M. The result data (Table 2) reveal that the values of k_{obs} show ~3.5-fold acceleration effect with varying spacer length from 3 to 12. On the other hand, 12py-*n*-py12.2Cl$^-$ micelles 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, cmc's, etc. of gemini micellar aggregates [46–48], 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 behavior 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 a 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.

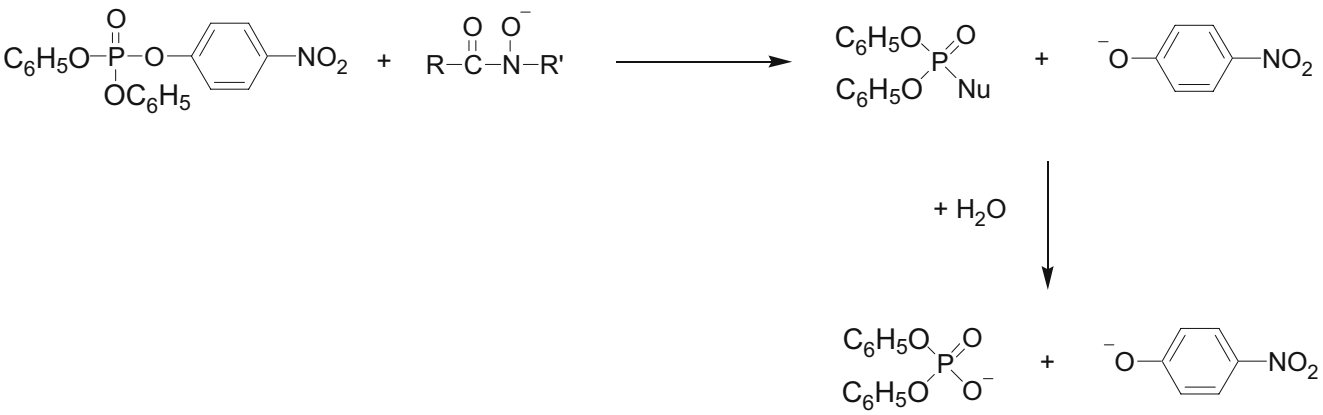
We may therefore conclude that among all gemini surfactants, 16-*12*-16,2Br$^-$ and 12py-4-12py,2Cl$^-$, dicationic surfactants are better catalyst for the hydrolytic reaction of PNPA, probably because the spacer decreases the extent of water penetration at the aggregate surface. The nucleophilic reaction of PNPA and PNPDPP are assisted by a decrease in the water content of the reaction environment. Menger et al. [49] have used chemical trapping to estimate concentration of H_2O and Br$^-$ at the surface of gemini micelles and concluded that proximity of the positive charges increases anion binding at the expense of binding of H_2O, 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$^-$ and dodecylpyridinium chloride for the 12py-4-12py,2Cl$^-$) [61].

However, the change of length of spacer has little effects on k_{obs}, although it has major effects on solubility of ammonium gemini surfactants [50].

Catalytic cleavage of PNPDPP in gemini micelles

When solublized in pH 9.1 micellar 16-12-16,2Br$^-$ and 12py-4-py12,2Cl$^-$, hydroxamate ions are an efficient catalyst for the cleavage of PNPDPP. The actual source of catalytic power is the α-nucleophilicity of the hydroxamate ion, which appears to be a 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 2.

Table 3 summarizes the k_{obs} values for the nucleophilic reaction of PNPDPP with hydroxamate ions in aqueous and gemini micellar media. The catalysis of the cleavage of PNPDPP (1.0×10^{-4} M) by hydroxamate ion is accelerated by the factor ~4.0 to tenfold in the absence of micellar aggregate, as thek^0_{obs} value for the background reaction of PNPDPP under the buffered condition is 0.03×10^{-3} s^{-1}. Thek^0_{obs} value for the hydrolytic background reaction is quite in agreement with the rate 0.0291×10^{-3} at pH 9.0 reported by Moss and Ihara [51]. From Table 3, 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 PNPDPP by the different hydroxamate ions. The 16-*12*-16,2Br$^-$ micelle showed 73-fold catalysis with the *N*-phenylbenzohydroxamate ion ($1.0\times$



Scheme 2 Catalytic cleavage of PNPDPP in gemini micelles by hydroxamate ions

Table 3 Rate constants (k_{obs}, s^{-1}) for the hydrolysis of PNPDPP catalyzed by various hydroxamate ions in gemini micelles[a]

[gemini] m*M*	$k_{obs}\times10^3$ (s^{-1})					
	16-*12*-16,2Br^-			12py-4-py12,2Cl^-		
	BHA	PBHA	BHA	SHA	MCBHA	PBHA
0	0.15	0.13	0.15	0.19	0.34	0.13
0.53	–	1.74	1.06	1.09	2.82	3.30
0.75	–	–	–	–	–	6.32
1.00	0.79	1.90	1.13	1.14	3.87	7.47
1.60	0.87	2.19	1.27	1.28	4.45	7.67
3.74	0.64	1.87	1.18	–	4.00	7.10
5.00	0.60	1.58	1.18	1.17	3.84	7.01

[a] Conditions: 0.06 M borate buffer, pH=9.1, 27 °C; [PNPDPP]=1.0×10^{-4} M, [HA]=1.0×10^{-3} M, Reaction medium 3.3% MeCN, $k^0_{obs}=0.030\times10^{-3}$ s^{-1} (k^0_{obs} is the value of hydrolytic background reaction in buffer condition)

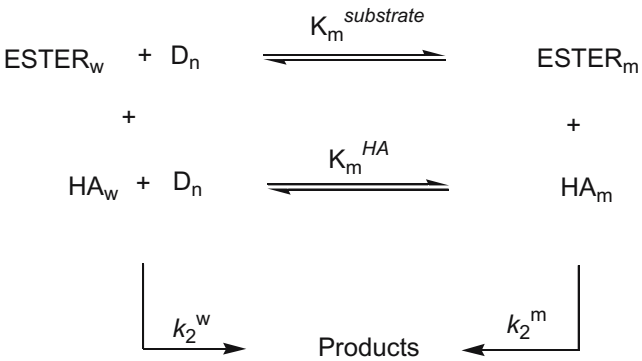
10^{-3} M). Under the identical concentration of 12py-*4*-py12,2Cl^-, the micelle showed 255-fold rate enhancement. It is also interesting to note that the pyridinium-based gemini is threefold more reactive than the ammonium-based gemini surfactant.

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 [51–53]. 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 PNPDPP 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^{max}_{obs} caused a decrease in the reaction rate possibly because of 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 *N*-methyl-2-chlorobenzohydroxamic acid (MCBHA) for the cleavage of PNPDPP. The pK_a value of the MCBHA is 7.65 and hence ionizes significantly as reactive hydroxamate ion compared to the PBHA (pK_a 8.9). Therefore, MCBHA must be more reactive than PBHA because of the electrostatic attraction into the cationic micelles. Surprisingly, PBHA shows larger rate acceleration effect because of the hydrophobic as well as electrostatic attraction into the micelles. We observed similar results for the nucleophilic dephosphorylation reaction of PNPDPP with many *N*-substituted and unsubstituted hydroxamate ions in the cetylpyridinium bromide micelle [27–31]. Such reactivity patterns have also been observed by Morales-Rojas and Moss [54] while studying the nucleophilic reactivity of the iodosyl nucleophiles with varying hydrophobicity of the nucleophiles in CTA^+ micelle. The data in Table 3 reveals that the hydrophobicity of hydroxamate nucleophile greatly influences its reactivity.

Applications of the pseudophase model

Quantitative treatments of reactivity in association colloids frequently use the pseudophase model, which predict that values of k_{obs} will increase (or decrease) monotonically and become constant with the fully bound substrate [55–57]. Reagents that are partitioned into the micelles can react in the interfacial region, which is regarded as a pseudophase distinct from the bulk solvent. Depending upon the interaction of substrate into the micelle, the rate of reaction is accelerated or inhibited. The influence of gemini micelles on the k_{obs} values for the nucleophilic bimolecular reactions of PNPA and PNPDPP with hydroxamate ions can be described as illustrated in Scheme 3.



Scheme 3 Nucleophilic bimolecular reactions of PNPA and PNPDPP with hydroxamate ions

In Scheme 3, subscripts w and m indicate aqueous and micellar pseudophases, respectively, and D_n represents the micellized surfactant, that is, $[D_n]=[D]_T-cmc$, 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 two pseudophases is expressed by means of the following expression:

$$K_m^{HA} = \frac{[HA]_m}{[HA]_w[D_n]} \tag{3}$$

By means of a simple balance of matter, we can obtain the following expressions for the HA concentration:

$$[HA]_w = \frac{[HA]_T}{\left(1 + K_m^{HA}[D_n]\right)} \quad [HA]_m = \frac{[HA]_T K_m^{HA}[D_n]}{\left(1 + K_m^{HA}[D_n]\right)} \tag{3.1}$$

The distribution constant of the ESTER is:

$$K_m^{ESTER} = \frac{[ESTER]_m}{[ESTER]_w[D_n]} \tag{3.2}$$

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

$$[ESTER]_w = \frac{[ESTER]_T}{\left(1 + K_m^{ESTER}[D_n]\right)}$$
$$[ESTER]_m = \frac{[ESTER]_T K_m^{ESTER}[D_n]}{\left(1 + K_m^{ESTER}[D_n]\right)} \tag{3.3}$$

The rate equation is:

$$\text{rate} = k[ESTER]_T[HA]_T \tag{3.4}$$

$$\text{rate} = k_{obs}[ESTER]_T \tag{3.5}$$

Equation 3.4 can be rewritten as:

$$\text{rate} = \text{rate}_w + \text{rate}_m \tag{3.6}$$

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

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

$$k_{obs} = \frac{k_2^w + \frac{k_2^m}{\overline{V}} K_m^{ESTER} K_m^{HA}[D_n]}{\left(1 + K_m^{ESTER}[D_n]\right)\left(1 + K_m^{HA}[D_n]\right)}[HA]_T \tag{3.7}$$

Scheme 3 considers the distribution of PNPA and PNPDPP between the aqueous and micellar pseudophases, K_m^{PNPA} and K_m^{PNPDPP}. The association constants of PNPA and PNPDPP have been obtained from fitting the reaction data with the values of $K_m^{PNPA}=185\ M^{-1}$ and $K_m^{PNPDPP}=1200\ M^{-1}$ in 16-12-16.2Br^- and $K_m^{PNPDPP}=2{,}500\ M^{-1}$ in 12py-*4*-py12.2Cl^- gemini micelles. The distribution of the hydroxamate ion, HA, between both pseudophases is considered through the distribution constant K_m^{HA}. The different reactivities in the aqueous and micellar pseudophases 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 $\overline{V}$ equal to the partial molar volume of the interfacial reaction region in the micellar pseudophase, determined by Bunton et al. [58] as 0.14 $dm^3\ mol^{-1}$. Micellar binding of both substrate, PNPA and PNPDPP, 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 4 allow us to study the influence of the nature of the micelle for the reaction of PNPA with unsubstituted and *N*-substituted hydroxamate ion. From the fitting of Eq. 3.7, we obtained $k_2^m=4.46\times10^{-1}$ and $2.13\times10^{-1}\ M^{-1}\ s^{-1}$ for the highly reactive gemini micellar systems (MCBHA/12py-*4*-py12.2Cl^- and PBHA/12py-*4*-py12.2Cl^-). Likewise, we a obtained value of $k_2^m=3.02\times10^{-1}\ M^{-1}\ s^{-1}$, for the BHA/12py-*4*-py12.2Cl^- and $k_2^m=2.28\times10^{-2}\ M^{-1}\ s^{-1}$ for the BHA/16-*12*-16.2Br^-

Table 4 Kinetic parameters obtained by applying pseudophase model for the nucleophilic reaction of PNPA with hydroxamate ions in the presence of 12py-4-py12,2Cl^- and 16-*12*-16,2Br^- micelles

Hydroxamate	k_2^w ($M^{-1}\ s^{-1}$)	K_m^{PNPA} (M^{-1})	K_m^{HA} (M^{-1})	k_2^m ($M^{-1}\ s^{-1}$)
AHA	1.87	185	325	$1.82\pm0.09\times10^{-2}$
BHA	5.40	185	40	$3.02\pm1.72\times10^{-1}$
	[a]5.40	[a]185	[a]30	[a]$2.28\pm0.28\times10^{-2}$
MCBHA	2.15	185	25	$4.46\pm0.50\times10^{-1}$
PBHA	3.68	185	135	$2.13\pm0.16\times10^{-1}$

a=Kinetic parameters for the reactions in 16–12–16.2Br⁻ micelle.
Conditions: 0.06 M phosphate buffer, pH=7.9, μ=0.1 M KCl.

Table 5 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[a]

Surfactant	HA	k_2^w (M^{-1} s^{-1})	K_m^{PNPDPP} (M^{-1})	K_m^{HA} (M^{-1})	k_2^m (M^{-1} s^{-1})
16-*12*-16,2Br$^-$	BHA	0.15	1200	370	$7.28\pm0.70\times10^{-4}$
16-*12*-16,2Br$^-$	PBHA	0.13	1200	315	$2.16\pm0.17\times10^{-3}$
12py-*4*-py12,2Cl$^-$	BHA	0.15	2500	75	$3.12\pm0.59\times10^{-3}$
12py-*4*-py12,2Cl$^-$	MCBHA	0.34	2500	70	$1.15\pm0.34\times10^{-2}$
12py-*4*-py12,2Cl$^-$	PBHA	0.13	2500	85	$1.79\pm0.50\times10^{-2}$
12py-*4*-py12,2Cl$^-$	SHA	0.19	2500	80	$3.04\pm0.56\times10^{-3}$

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

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 PNPDPP can explain the reactivity pattern of the hydroxamate ions in both the gemini micellar media. Table 5 summarizes the values of K_m^{PNPDPP}, K_m^{HA}, and k_2^m for the reaction of PNPDPP. Simulated rate surfactant profiles for PNPDPP are shown in Figs. 3 and 4. 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 5 and Figs. 3 and 4 also support the observation that the gemini surfactant with the pyridinium head group is more reactive than gemini with the ammonium head group. Further support for the differential reactivity can be obtained from the comparison of the values of k_2^m at the micellar interface. The 12Py-4-py12,2Cl$^-$ micelle shows approx. eightfold and approx. fourfold catalytic advantage than 16-12-16,2Br$^-$ micelles for the reaction of PNPDPP with PBHA and BHA, respectively. An alternative explanation can be given with assumption: (a) a large incorporation of PNPDPP in the gemini surfactant of the pyridinium head group, (b) effective nucleophilicity of PBHA in the presence of the gemini surfactant, and (c) ready exchangeability of the Cl$^-$ counterion than Br$^-$. The large value for association constant of PNPDPP in gemini pyridinium micelles can be supported by the ability of aromatic rings to stack on pyridinium rings [59]. The orientation of PNPDPP in the pyridinium gemini surfactant–hydroxamate can be described by the model presented by Balakrishnan et al. [60] for the case of monomeric 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 strong degree of counterion binding [61]. The combination of the two interactions can lead to a high binding of the hydroxamate ions, thus exchanging with the chlorides.

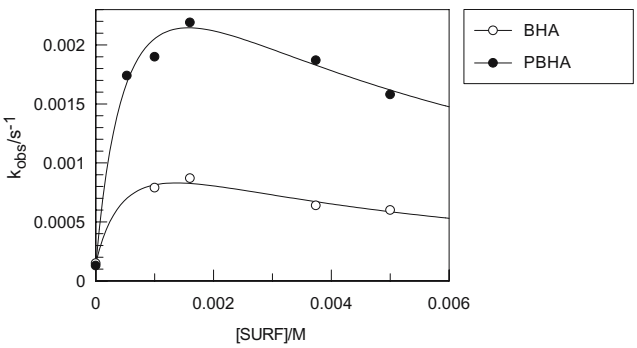


Fig. 3 Simulated rate-surfactant profiles for the reaction of *p*-nitrophenyl diphenyl phosphate with benzohydroxamate and *N*-phenylbenzohydroxamate ions in 16-12-16,2Br$^-$ gemini surfactant (*lines* are predicted values with model)

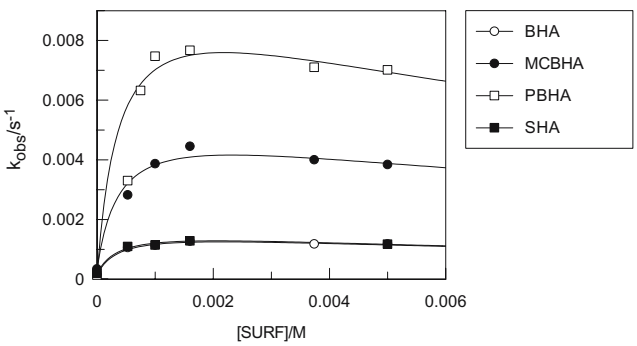


Fig. 4 Simulated rate-surfactant profiles for the reaction of *p*-nitrophenyl diphenyl phosphate with hydroxamate ions in 12Py-*4*-py12,2Cl$^-$ gemini surfactant (lines are predicted values with model)

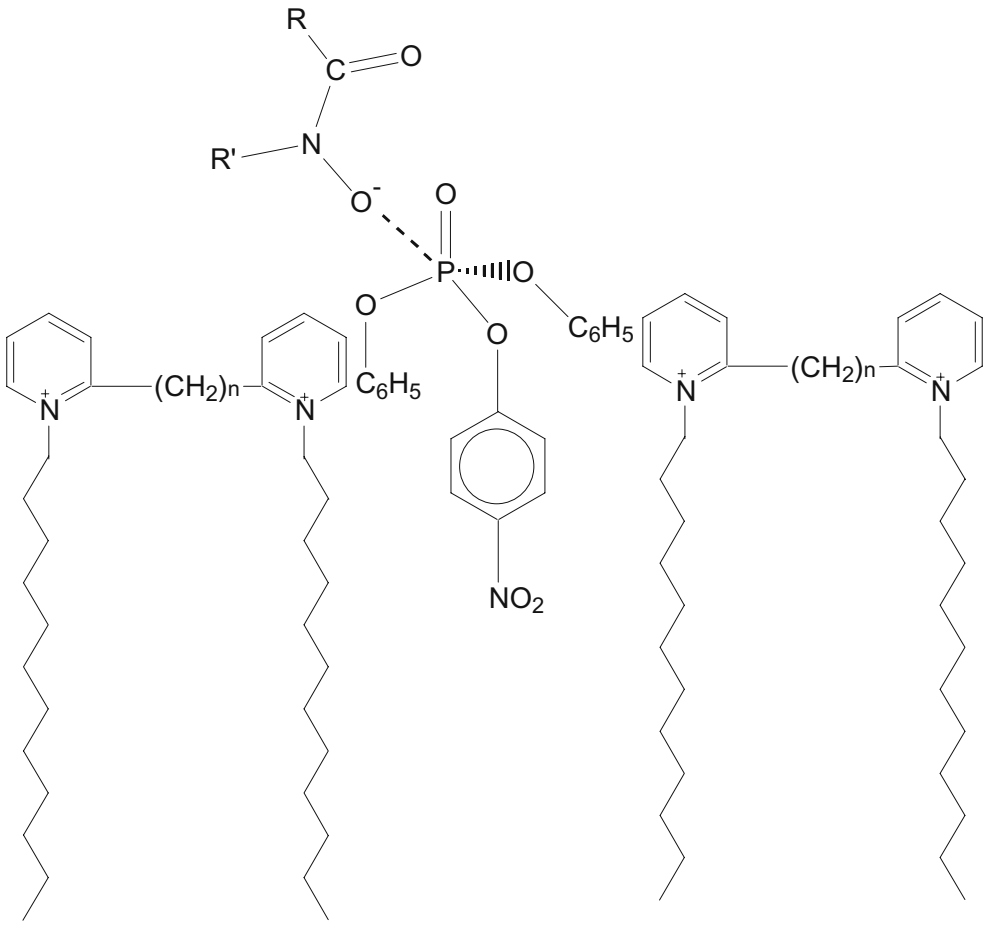


Fig. 5 Depiction of *p*-nitrophenyl diphenyl phosphate and hydroxamate orientations at micellar interface of 12py-n-py12.2Cl$^-$ gemini micelle

The nucleophilic reactions in micelles are generally governed by basicity and the incorporation of different nucleophiles into the micelle (Fig. 5).

Conclusions

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 PNPA and PNPDPP using α-nucleophile hydroxamate ions in the presence of gemini surfactants with quarternary ammonium bromide and pyridinium chloride head groups. Pyridinium gemini surfactants show higher reactivity than trimethylammonium ones. The arrangement of different head groups at the micellar surface can leave a different space for the reactant to attach (first) and enter (in a second time) the micelle. The phenyl ring of the reactant can stack between the pyridinium ring because of 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.

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.

Experimental section

Materials *N*-Phenylbenzohydroxamic acid and benzohydroxamic were prepared by the literature method [62, 63]. MCBHA was synthesized by the reaction of 2-chlorobenzoyl chloride and *N*-methyl hydroxylamine hydrochloride. The ether solution of 2-chlorobenzoyl chloride (0.05 mol) and *N*-methyl hydroxylamine hydrochloride (0.01 mol) was stirred at room temperature in the presence of sodium carbonate (0.01 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 acetohydroxamic acid, were obtained from Sigma/Aldrich. PNPDPP was prepared and purified by the literature method [64]. All the samples of pyridinium gemini surfactants were the same as reported in a previous paper [47]. Ammonium gemini surfactants were prepared according to well-established protocols [46–50].

Kinetics All of the reactions were followed at 27±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 PNPDPP were determined by following the increase in absorption of the *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 absorbance/time result fit very well to the first-order rate Eq. 4:

$$\ln(A_\infty - A_t) = \ln(A_\infty - A_o) - kt \quad (4)$$

The pseudo-first-order rate constants can be determined by least squares fits. Each experiment was repeated at least twice, and the observed rate constant was 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 Systronics (type-335) pH meter.

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