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Comparative studies on reaction of bis(*p*-nitrophenyl) phosphate and α-nucleophiles in cationic micellar media

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We studied the cleave of bis(*p*-nitrophenyl) phosphate (BNPP) over a pH range of 7.0–12.0 in the presence of cationic micelles of cetyldiethylethanolammonium bromide, cetyldimethylethanolammonium bromide, cetylpyridinium bromide, cetyltrimethylammonium bromide, and cetylpyridinium chloride by using different α-nucleophiles, *viz* acetohydroxamate, benzohydroxamate, salicylhydroxamate, butane-2,3-dione monooximate, and α-benzoin oximate ions. With the use of α-nucleophiles in cationic micellar media, the hydrolytic cleavage of BNPP was found to be approximately 10^5-fold faster than its spontaneous hydrolysis. All reactions followed pseudo-first-order kinetics. The effect of various concentrations of cationic micelles for the reaction of BNPP and α-nucleophiles has been studied. The variation of k_{obs} values of the reactions depends on the micellar structure, that is, head groups, hydrophobic tail length, and counter ion. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this paper.

Keywords: bis(*p*-nitrophenyl) phosphate; cationic micelle; micellar catalysis; pH; α-nucleophiles

INTRODUCTION

Hydrolysis and nucleophilic substitution reactions of phosphoesters are involved in many biological processes.[1] Extensive studies have been attempted to understand the mechanism of such crucial reactions.[2–4] Phosphodiesters are extremely stable compounds and are highly resistant toward hydrolytic cleavage at physiological pH. This high stability is in agreement with the fundamental role of DNA in the preservation of genetic information and underscores the importance of studies on the mechanism of phosphodiester hydrolysis.[5–8] Many α-nucleophiles such as hydroxylamine,[9] hydrazine,[10] hydroxamic acid,[4,11] and oxime[12] are truly effective dephosphorylating agents for phosphodiesters and triesters. There are unshared electron pairs on the atom adjacent to the nucleophilic center of these α-nucleophiles. The hydrolysis of triester by α-nucleophiles in different micellar media is a widely studied reaction.[13–23] It has been observed that cationic micellar media accelerate the reactivity of α-nucleophiles.[24–26] Kinetic aspect of micellar catalysis[27,28] represents a significant contribution to the observed rate in this case of hydrolysis. Micellar rate effects have been quantitatively determined on the basis of pseudophase models[29,30] that high local concentrations of nucleophiles are largely responsible for the rate acceleration in the interfacial micellar region.[26] It was observed that cationic micelles accelerate the spontaneous hydrolysis of bis(*p*-nitrophenyl) phosphate (BNPP) up to 2×10^5-fold[31] and accelerate the reaction of hydroxamates and phosphate triesters.[26–28,30] We herein examined micellar effects on the reactions of the less reactive phosphodiester with simple hydroxamates (Scheme 1). Different hydroxamate ions [acetohydroxamate (AHA^-), benzohydroxamate (BHA^-), and salicylhydroxamate (SHA^-)] and oximate ions [butane-2,3-dione monooximate ($BDMO^-$) and α-benzoin oximate] have been used. It has been proved that hydroxamic acid behaves as a self-destructive intramolecular scissor, which reacts and loses nucleophilic ability after reaction.[4] Cheng *et al.*[31] have studied one of the most effective metallomicellar (Cu^{2+}–CTAB) systems for hydrolysis of BNPP. They found that kinetic rate data k_{obs}, $3.23 \times 10^{-5}\,s^{-1}$ (buffer + CTAB) at pH 7.12, has over approximately 10^5-fold acceleration, with micellar media, than spontaneous hydrolysis. It is well known that micelles and similar colloidal assemblies generally increase the nucleophilic reactivity.[32] The structure and properties of surfactants play an important role in determining chemical reactivity.

In this article, we describe the comparative analysis of the nucleophilicity of α-nucleophiles such as oximate and hydroxamate ions toward the reaction of BNPP in the presence of some cationic surfactants at 27 °C (Chart 1). BNPP is very slow toward hydrolysis so that any hydrolytic scheme developed for the diester is likely to be useful for actual target compound. Therefore, this original work on the BNPP hydrolytic cleavage in a micellar system will provide a better understanding of the hydrolytic aspect of phosphate diesters. The roles of pH and pK_a of α-nucleophiles and the effect of surfactant head group, chain length variation, and counter ion have been discussed.

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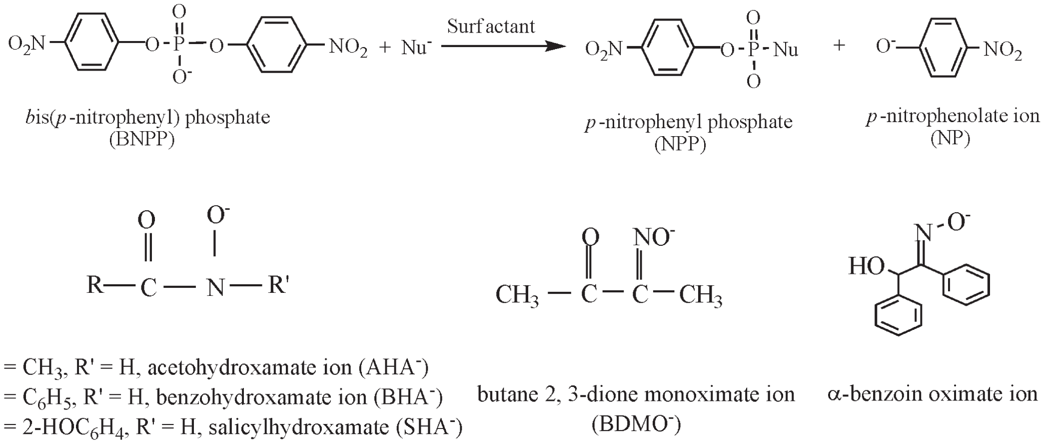


Scheme 1. Nucleophilic reaction of bis(p-nitrophenyl) phosphate with α-nucleophiles

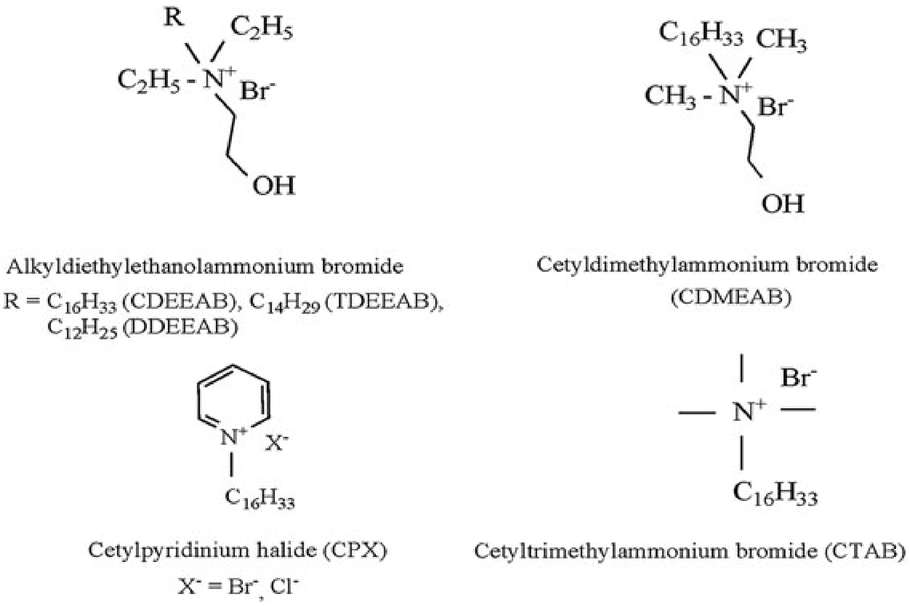


Chart 1. Cationic surfactants

EXPERIMENTAL

Materials

The phosphate diester, that is, BNPP, was procured from Sigma-Aldrich (St. Louis, MO, USA). Acetohydroxamic acid, benzohydroxamic acid, salicylhydroxamic acid, butane-2,3-dione monoxime, and α-benzoin oxime were procured from Sigma-Aldrich. Cetyldiethylethanolammonium bromide (CDEEAB), tetradecyldiethylethanolammonium bromide (TDEEAB), dodecyldiethylethanolammonium bromide (DDEEAB), and cetyldimethylethanolammonium bromide (CDMEAB) were obtained from the laboratory of Prof. R. M. Palepu (retd. professor), St. Francis Xavier University, Antigonish, Canada. Cationic surfactants, that is, cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPB), and cetylpyridinium chloride (CPC), were obtained from Sigma-Aldrich. All solutions were prepared in triply distilled water.

Method

The reactions were studied spectrophotometrically using Systronics Ahmedabad (Naroda Gidc), India (Types 104 and 118) spectrophotometer by monitoring the appearance of the leaving *p*-nitrophenolate ion at 400 nm and 27 °C ± 0.2 °C. All kinetic experiments were performed at an ionic strength of 0.1 M (with KCl). Borate buffer was employed to control the pH of the reaction media. All the pH measurements were obtained using Systronics (Type 335) pH meter. The reactions were initiated by adding 100 μL of a stock solution of the BNPP (0.005 M) in an aqueous buffer solution containing other reactants. Nucleophile concentration was taken in large excess over the substrates assuring pseudo-first-order kinetics. The observed first-order rate constants (k_{obs}) were calculated by a nonlinear least squares fitting of the absorbance versus time result fit very well to the first-order rate equation.

$$\ln(A_\infty - A_t) = \ln(A_\infty - A_0) - kt \qquad (1)$$

RESULT AND DISCUSSION

The first-order rate constants, k_{obs}, for the reaction of BNPP with AHA, BHA, SHA, BDMO, and α-benzoin oxime have been measured

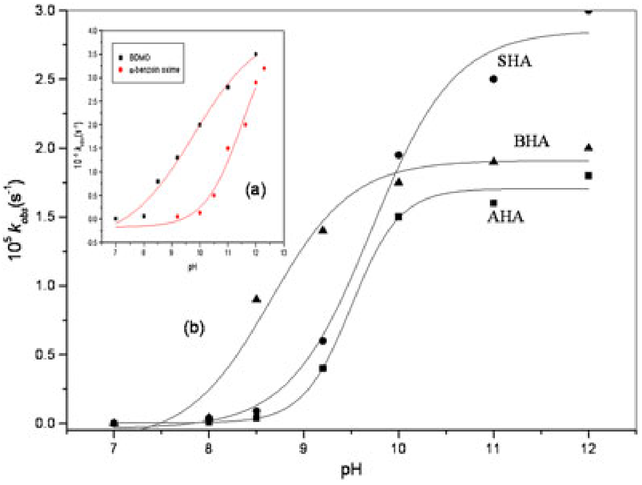


Figure 1. Plots of first-order rate constants versus pH for the reaction of BNPP with insect (a) oximate ions and (b) hydroxamate ions in CDEEAB (2.0×10^{-3} M)

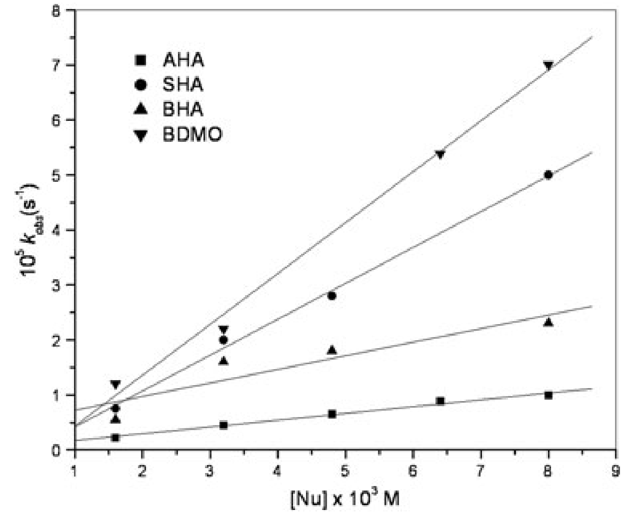


Figure 2. Kinetic plots of k_{obs} versus concentration of [Nu] for the reaction of BNPP at pH 11

spectrophotometrically under pseudo-first-order conditions in the absence and the presence of cationic surfactants at 27 °C and pH 11.0. Figure 1 illustrates the pH-rate profile for the dephosphorylation of BNPP by various α-nucleophiles at pH 7.0–12.0 (Table 1), in the presence of CDEEAB, where k_{obs} increases with pH and reaches a maximum in the pH region where AHA, BHA, SHA, BDMO, and α-benzoin oxime are fully deprotonated. The apparent dissociation constants (pK_a) 8.64, 9.71, 9.50, 9.78, and 11.5 for AHA, BHA, SHA, BDMO, and α-benzoin oxime, respectively, in CDEEAB (2.0×10^{-3} M), at constant $[Nu] = 1.6 \times 10^{-3}$ M (Fig. 1), gives a rate constant in the plateau region of $0.40 \times 10^{-5}\,s^{-1}$, $1.95 \times 10^{-5}\,s^{-1}$, $1.75 \times 10^{-5}\,s^{-1}$, $2.00 \times 10^{-5}\,s^{-1}$, and $1.10 \times 10^{-5}\,s^{-1}$. The first-order rate constant for the hydrolysis of BNPP by hydroxide ion at pH 11.0 is about $3.28 \times 10^{-9}\,s^{-1}$.[33–37] Table 2 indicates the kinetic rate data for the reaction of BNPP with different concentrations of BDMO, α-benzoin oxime, AHA, BHA, and SHA at pH 11.0. It is found that α-nucleophiles in cationic micellar media display significant catalytic activity for the cleavage of BNPP (Table 2). Kinetic data show additional support for the hypothesis that hydroxamate and oximate ions are acting as a nucleophilic catalyst for the reaction of BNPP. All the reactions followed rate Eqn 2:

$$k_{obs} = k_0 + k_{Nu^-}[Nu^-] \tag{2}$$

where $k_0 = k_{H_2O} + k_{OH^-}[OH^-]$.

It is assumed that catalysis by the nucleophile is dependent upon the ionization state of the hydroxamic acid and oxime. It is known that the anion of hydroxamate and oximate ions acts as a reactive species for the hydrolysis of phosphate esters (Fig. 2). The first-order rate constants and the calculated second-order rate constants are shown in Table 3. First-order rate constants are much greater than those of the spontaneous water reaction of BNPP (k_0) $1.1 \times 10^{-11}\,s^{-1}$; that is, there is up to 10^5-fold rate enhancement, typical of α-nucleophiles. Under the physiological condition, the reaction of BNPP with oximate and hydroxamate ions is slow.

Table 1. pH effects on pseudo-first-order rate constants for the reaction of BNPP with different α-nucleophiles in CDEEAB (2.0×10^{-3} M)

pH	$10^5\,k_{obs}\,(s^{-1})$				
	AHA	BHA	SHA	BDMO	α-benzoin oxime
7.0	—[1]	—[1]	—[1]	—[1]	—
8.0	0.009	0.04	0.04	0.06	—
8.5	0.04	0.09	0.90	0.80	—
9.2	0.40	0.60	1.40	1.30	0.05
10.0	1.50	1.95	1.75	2.00	0.13
10.5	—	—	—	—	0.50
11.0	1.60	2.60	1.90	2.80	1.10
11.6	—	—	—	—	2.00
12.0	1.80	3.00	2.00	3.50	2.90
12.3	—	—	—	—	3.20

Reaction condition: temp. = 27 °C, $[BNPP] = 1.6 \times 10^{-4}$ M, $[Nu] = 1.6 \times 10^{-3}$ M, $\mu = 0.1$ M KCl, $[CDEEAB] = 2 \times 10^{-3}$ M.

[1] Very slow.

Kinetic studies in cationic micellar media

The hydrolysis of BNPP at pH 11.0 in cationic micelles of CDEEAB, CDMEAB, CPB, CTAB, and CPC with AHA, BHA, SHA, BDMO, and α-benzoin oxime is much faster than α-nucleophiles alone (Tables 4 and 5). Rate–surfactant profiles for the hydrolytic cleavage of BNPP with various cationic surfactants are shown in Fig. 3. For the observed first-order rate constant, k_{obs} during BNPP cleavage catalyzed by AHA, BHA, SHA, BDMO, and α-benzoin oxime in cationic surfactants increased with increasing concentration of surfactants, reached a maximum value, and then decreased with increasing concentration of surfactants from 0.001 to 0.020 M (Figs. 3–5 and S1 and S2). At the rate maxima, the first-order rate constants, k_{obs}, for the reaction of BNPP with CDEEAB-bound BDMO$^-$, SHA$^-$, BHA$^-$, AHA$^-$, and α-benzoin oximate ions are approximately $8.4 \times 10^{-5}\,s^{-1}$, $4.6 \times 10^{-5}\,s^{-1}$, $5.7 \times 10^{-5}\,s^{-1}$, $3.2 \times 10^{-5}\,s^{-1}$, $2.6 \times 10^{-5}\,s^{-1}$, at pH 11.0 (Tables 4 and 5). It has been already proved that cationic surfactants accelerate the reaction. The electrostatic attraction of cationic head

Table 2. Effect of nucleophilic concentration of various α-nucleophiles on pseudo-first-order rate constant for the reaction of BNPP in the absence and the presence of cationic surfactant

[Nu], (mM)	$10^5\,k_{obs}$ (s^{-1})								
	Nil				Surfactant				
	AHA	BHA	SHA	BDMO	AHA	BHA	SHA	BDMO	α-benzoin oxime
1.6	0.22	0.55	0.75	1.20	1.60	2.50	1.90	2.80	1.10
3.2	0.45	1.60	2.00	2.20	3.00	4.00	3.30	4.50	2.10
4.8	0.65	1.80	2.80	—	4.20	6.30	5.00	6.50	3.00
6.4	0.88	—	—	5.39	6.00	7.00	6.50	7.80	4.00
8.0	0.99	2.30	5.00	7.01	—	—	—	—	—

Reaction conditions: temp. = 27 °C, [BNPP] = 1.6×10^{-4} M, pH = 11.0, $\mu = 0.1$ M KCl, [CDEEAB] = 2.0×10^{-3} M.

Table 3. The observed first-order and second-order kinetic rate data for the BNPP cleavage with various α-nucleophiles in the absence and the presence of CDEEAB surfactants

Nucleophiles	Nil		Surfactant	
	k_{obs} (s^{-1})	k_2 ($M^{-1}\,s^{-1}$)	k_{obs} (s^{-1})	k_2 ($M^{-1}\,s^{-1}$)
k_0	1.1×10^{-11} (from Refs. [34,35])	—	—	—
k_{OH}	3.9×10^{-9}	3.50×10^{-5} (from Refs. [36,37])	—	—
AHA	0.22×10^{-5}	1.20×10^{-3}	1.60×10^{-5}	9.00×10^{-3}
BHA	0.55×10^{-5}	2.40×10^{-3}	2.50×10^{-5}	9.80×10^{-3}
SHA	0.75×10^{-5}	6.50×10^{-3}	1.90×10^{-5}	9.67×10^{-3}
BDMO	1.20×10^{-5}	9.20×10^{-3}	2.80×10^{-5}	1.06×10^{-2}
α-benzoin oxime	—	—	1.10×10^{-5}	6.00×10^{-3}

Reaction conditions: temp. = 27 °C, [BNPP] = 1.6×10^{-4} M, [Nu$^-$] = 1.6×10^{-3} M, $\mu = 0.1$ M KCl, pH = 11.0, [CDEEAB] = 2.0×10^{-3} M.

Table 4. Kinetic data for the reaction of BNPP with hydroxamate ions in micellar media

Surfactant (mM)	$10^5\,k_{obs}$ (s^{-1})														
	AHA					BHA					SHA				
	CPC	CPB	CDEEAB	CDMEAB	CTAB	CPC	CPB	CDEEAB	CDMEAB	CTAB	CPC	CPB	CDEEAB	CDMEAB	CTAB
0.00	0.22	0.22	0.22	0.22	0.22	0.55	0.55	0.55	0.55	0.55	0.75	0.75	0.75	0.75	0.75
1.00	—	—	—	—	—	4.35	2.75	2.60	1.60	2.20	2.00	1.90	1.80	1.70	1.80
2.00	2.58	2.34	1.34	2.52	1.11	6.00	3.50	4.85	4.10	3.00	2.40	2.06	3.50	3.23	3.00
5.00	3.41	3.32	3.27	2.77	1.52	6.82	5.60	5.75	5.02	3.80	6.20	5.73	4.60	3.60	3.20
10.0	2.42	2.1	2.4	2.2	1.2	5.90	3.80	3.62	3.43	1.80	5.80	5.00	4.10	3.40	2.10
20.0	—	—	—	—	—	3.80	3.20	3.10	2.50	1.70	4.92	4.51	3.23	3.01	2.00

Reaction conditions: temp. = 27 °C, pH = 11.0, [BNPP] = 1.6×10^{-4} M, [Nu] = 1.6×10^{-3} M, $\mu = 0.1$ M KCl.

Table 5. Kinetic data for the reaction of BNPP with oximate ions in cationic micellar media

Surfactant (mM)	$10^5\ k_{obs}\ (s^{-1})$									
	BDMO					α-benzoin oxime				
	CPC	CPB	CDEEAB	CDMEAB	CTAB	CPC	CPB	CDEEAB	CDMEAB	CTAB
0.00	1.21	1.21	1.21	1.21	1.21	0.31	0.31	0.31	0.31	0.31
1.00	—	2.90	1.60	0.80	—	—	—	0.91	—	0.42
2.00	5.50	3.50	2.80	2.20	1.57	2.05	1.83	1.10	1.00	0.55
5.00	9.50	7.50	8.40	6.80	2.87	2.98	2.33	2.60	2.45	0.78
10.0	3.40	4.00	3.40	2.79	2.1	1.98	2.29	2.25	2.7	0.58

Reaction condition: temp. = 27 °C, pH = 11.0, [BNPP] = 1.6×10^{-4} M, [Nu] = 1.6×10^{-3} M, $\mu = 0.1$ M KCl.

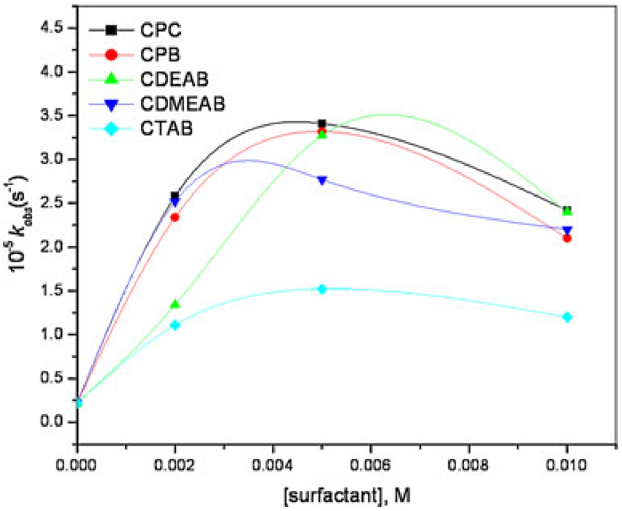


Figure 3. Plots of the kinetic rate data for the reaction of BNPP with AHA in borate buffer at pH 11 in various cationic surfactants

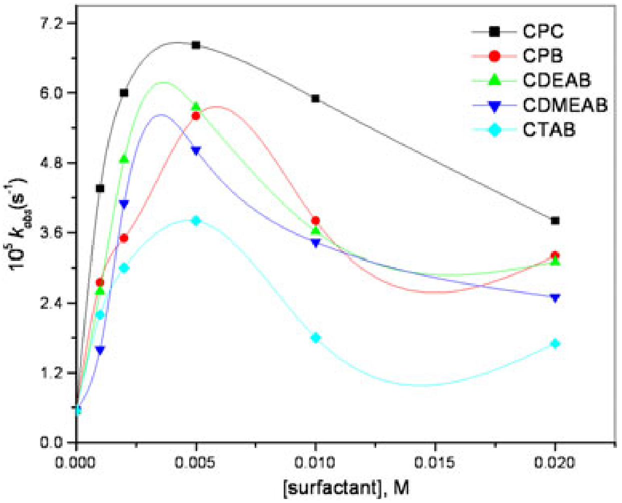


Figure 4. Plots of the kinetic rate data for the reaction of BNPP with BHA in borate buffer at pH 11 in various cationic surfactants

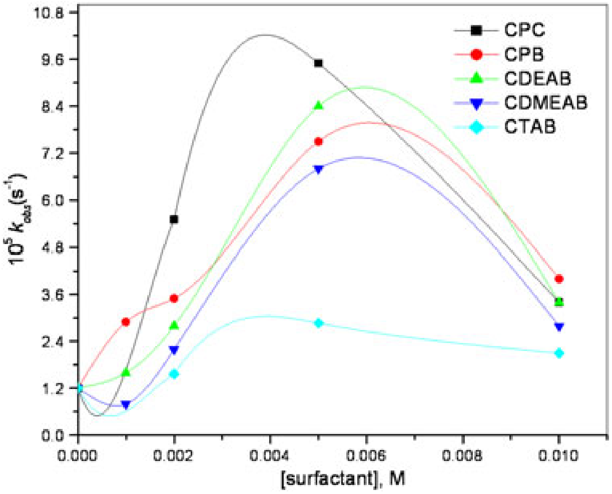
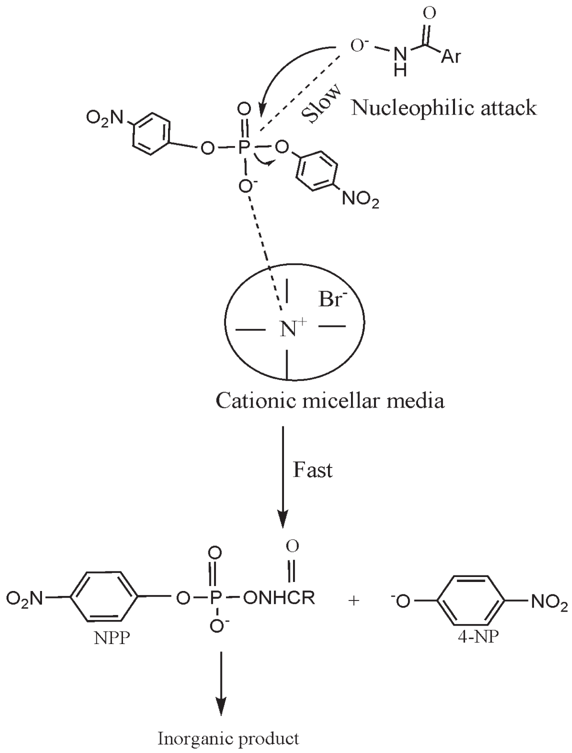


Figure 5. Plots of the kinetic rate data for the reaction of BNPP with BDMO in borate buffer at pH 11 in various cationic surfactants

groups of the surfactants at the micelle surface to the nucleophilic anion counterions leads to the increase of the local concentration of the nucleophile, whereas the incorporation of the substrate in the micelle leads to a higher local concentration of the reactants.[39] The rate of the hydrolysis should be mainly dependent on the concentration of BNPP and [Nu^-] in the cationic micellar media. As can be seen in Fig. 5, rate enhancement on the addition of surfactant would be expected to be more significant for the oximate ion ($BDMO^-$) compared with the hydroxamate ions (AHA^-, BHA^-, and SHA^-). This may be because the electrostatic interaction between the cationic micelle and the anionic oximate will be much larger than that between the cationic micelle and the hydroxamate ions. Hydroxamic acids have hydrophobic nature; therefore, the nucleophilicity of various hydroxamic acids is different. And an interesting phenomenon can be discovered – k_{obs} increased with increasing hydrophobicity of nucleophiles in micelles. This acceleration is due to (i) the hydrophobic and charge effects, which concentrate reagents in the cationic micelles, and (ii) the nucleophilicity of monoanionic AHA^-, BHA^-, SHA^- ions, which are effective α-effect nucleophiles with unshared electron pairs on oxygen and nitrogen. Moreover, the high nucleophilicity of oximate and hydroxamate ions is a typical behavior of α-nucleophiles. In our results, we found that BHA was slightly more hydrophobic than AHA and SHA, bound to cationic micelles hydrophobically as well as by electrostatic attraction, and has more efficient reaction with the bound substrate BNPP. It is considered that nucleophilicity is governed not only by the basicity but also by the strength of interaction between the nucleophile and the surfactant aggregate.[40] The marked increase in nucleophilicity in micellar media was observed in the order BDMO > SHA > BHA > AHA > α-benzoin oxime. The marked increase in micellar effects was observed in the order CPC > CPB > CDEEAB > CDMEAB > CTAB. In our previous work, the comparative catalytic reactivity of AHA^-, BHA^-, and SHA^- ions for the cleavage of triester (paraoxon)[13,14] and diester [bis(2,4-dinitrophenyl) phosphate (BDNPP)] by SHA in cationic micellar media has been studied. It has been observed that SHA showed remarkably enhanced catalytic efficiency for BDNPP in identical conditions: [BDNPP] = 1.0×10^{-4} M, [SHA] = 1.0×10^{-3} M, [KCl] = 0.1 M, [CTAB] = 2.0×10^{-3} M, pH 9.2 at 27 °C. Therefore, it is expected that the catalytic efficiency of the SHA^- is further enhanced in micellar microenvironments compared with BHA^- and AHA^- because of the active participation of dianionic species.[41]

Scheme 2 is outlined for the cleavage of phosphodiester BNPP with α-nucleophiles in cationic micellar medium. The experimental results show that the cleavage rate of BNPP is much smaller only in the presence of α-nucleophiles than in the cationic micelles due to the possible electrostatic repulsion between anionic phosphate ester and nucleophiles. The interaction of BNPP to the cationic micelles, both electrostatically and hydrophobically, facilitates the nucleophilic attack of anionic nucleophiles. Therefore, the true cause of the higher reactivity of BNPP cleavage in cationic micelles is attributed to the formation of plentiful substrate–nucleophile system. It is in agreement with similar work presenting 2-hydroxypropyl *p*-nitrophenyl phosphate (HPNP) cleavage in the presence of cationic micelles.[6] They observed ‘sandwich absorptive mode’ (micelle-HPNP-catalyst mode), in which the negative HPNP molecule is sandwiched in the interlayer between the positive micelle and the catalyst.[5,42–46]



Scheme 2. The sketch map of BNPP catalytic cleavage by α-nucleophiles in cationic micellar media

Effect of head group, chain length, and counter ion

The effect of different surfactant head groups such as the quaternary ammonium (CTAB) and pyridinium groups (CPB) on the hydrolysis of BNPP with hydroxamate and oximate ions has been studied. All the data are shown in Tables 4 and 5. The structure of surfactant head groups has an important role toward the molecular packing of organized self-assemblies.[47–49,40–42] An increase in the head group size leads to an increase in the interfacial area, and the space between two head groups is also enhanced.[43]

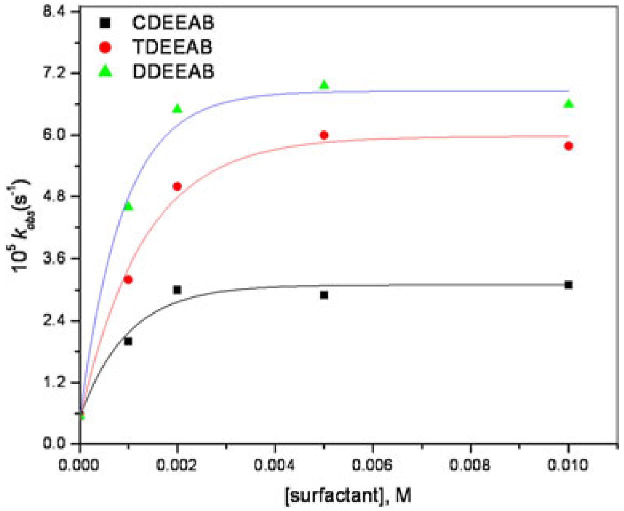


Figure 6. Plots of the kinetic rate data for the reaction of BNPP with BHA in borate buffer at pH 11 in various chain lengths of cationic surfactants

Table 6. Kinetic rate data for the reaction of BNPP with BHA and BDMO in borate buffer at pH 11.0 in chain length variation of cationic surfactants

Surfactant (mM)	$10^5\ k_{obs}\ (s^{-1})$					
	BHA			BDMO		
	DDEEAB	TDEEAB	CDEEAB	DDEEAB	TDEEAB	CDEEAB
0.00	0.55	0.55	0.55	1.21	1.21	1.21
1.00	2.00	3.20	4.60	3.50	4.20	4.60
2.00	3.00	5.00	6.50	4.30	5.80	6.50
5.00	3.20	6.00	6.96	5.50	7.20	8.40
10.0	2.90	5.79	6.60	4.80	6.10	7.20

Reaction conditions: temp. = 27 °C, [BNPP] = 1.6×10^{-4} M, [Nu] = 1.6×10^{-3} M, pH = 11.0, μ = 0.1 M KCl.

The space between two head groups allows the α-nucleophiles to solubilize itself smoothly at the interfacial region. Because of the enhanced interfacial region, the concentration of nucleophile and substrate increased and showed higher activity. There is little information about the effect of the variation of head groups on the micellar structure.[50–52] Table 4 clearly indicates that the nucleophilic activity of α-nucleophiles strongly depends on the structure and charge of the surfactant head group. In comparison, we found higher k_{obs} value with the pyridinium group (CPB), approximately 10.4-fold, than the quaternary ammonium group (CTAB), approximately 5-fold acceleration. The results indicate that specific interactions between the cationic surfactant and the nucleophile should be effective in determining the α-nucleophiles as the hydrophobicity together with the size of the head groups is increased. The variation of k_{obs} values of the reactions depends on the micellar structure, that is, head group, hydrophobic tail length, and counter ion. The rate constants in a variety of association colloids are slightly higher than in water and increase modestly with increasing micellar media involving variations in the surfactant tail groups and changes in the interfacial regions.[53] Analysis of kinetic data indicates that CDEEAB shows higher reactivity than CTAB. The increase of k_{obs} values with increasing alkyl chain lengths ($R = 12, 14, 16$) of the surfactants, that is, with increasing aggregation number of micelle, is mainly due to the increase in the electrical surface potential of the micelle and partially due to an increase in hydrophobicity of the palisade layer of the micelle. In all cases, the [CDEEAB] rate profile was maximum as compared with [TDEEAB] and [DDEEAB] surfactants because [CDEEAB] corresponds to complete solubilization of the substrate in the micellar pseudophase and because alkanol groups can exert a protective effect on the positive charge, thus lowering the attractive electrostatic interactions between the quaternary ammonium center of the micelle and the corresponding negative charge of the dissociated acid group in Table 6. The reactivity order follows the trend CDEEAB > TDEEAB > DDEEAB (Fig. 6 and S3).

Conclusion

In this study, we found that the nucleophilic activities of α-nucleophiles are higher with the cationic micellar media toward the BNPP cleavage. Experimental data show that the oximate ion ($BDMO^-$) has a higher catalytic activity compared with the hydroxamate ions (AHA^-, BHA^-, and SHA^-) in cationic micellar media. Among all the nucleophiles, CPC shows higher catalytic activity toward the hydrolytic cleavage of diester compared with CPB, CDEEAB, CDMEAB, and CTAB. The hydrolytic cleavage of diester is very slow; therefore, kinetic rate data are limited, but α-nucleophiles with cationic surfactants are better for BNPP cleavage. This study will help to elucidate the cleavage mechanisms of phosphodiester bonds and design of efficient artificial nucleases.

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