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Micellar-accelerated hydrolysis of organophosphate and thiophosphates by pyridine oximate

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Abstract

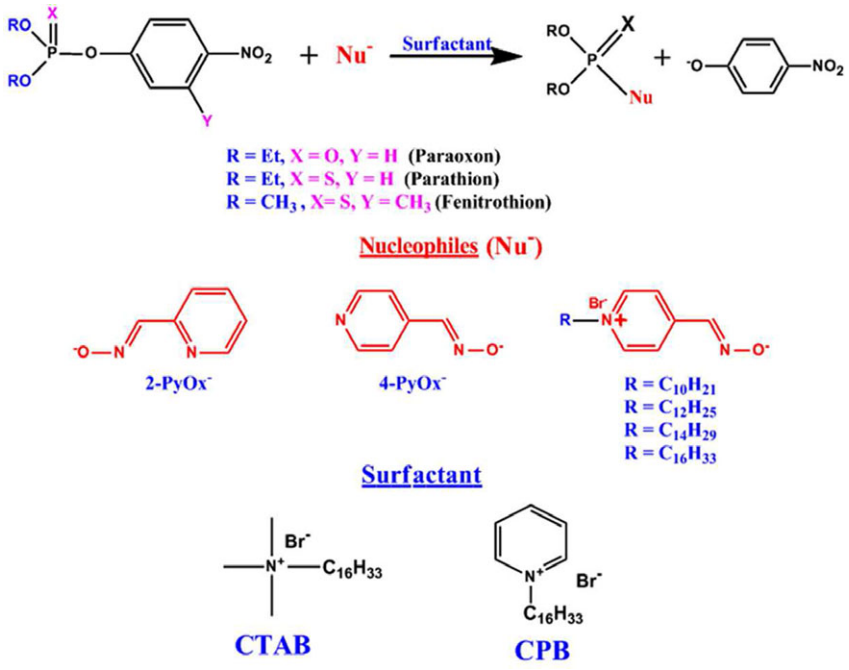
Rate constants for the hydrolysis reaction of phosphate (paraoxon) and thiophosphate (parathion, fenitrothion) esters by oximate (pyridinealdoxime 2-PyOx$^-$ and 4-PyOx$^-$) and its functionalized pyridinium surfactants 4-(hydroxyimino) methyl)-1-alkylpyridinium bromide ions (alkyl = C_nH_{2n+1}, n = 10, 12, 14, 16) have been measured kinetically at pH 9.5 and 27°C in micellar media of cationic surfactants cetyltrimethylammonium bromide (CTAB) and cetylpyridinium bromide (CPB). Acid dissociation constant, pK_a, of oximes has also been determined by spectrophotometric, kinetic, and potentiometric methods. The rate acceleration effects of cationic micelles have been explored. Cationic micelles of the pyridinium head group (CPB) showed a large catalytic effect than the ammonium head group (CTAB). The effects of pH, oximate concentration, and surfactants have been discussed.

KEYWORDS
cationic micelles, functionalized surfactants, oximate, phosphate esters

1 | INTRODUCTION

A flexible and rapid decontamination method has been devoted for detoxifying persistent organophosphorus pesticides as well as a chemical warfare agent over the past several decades.[1,2] Both pesticides and chemical warfare agents inhibit the serine moiety of the enzyme acetylcholinesterase and deactivate its capacity with significant impacts on the nervous system.[3] The inhibition results in life-endangering impairments on the human body such as cholinergic disorder, respiratory failure, and ultimately leading to death. Oximate (Ox$^-$) and hydroxamate (HA$^-$) were proved to be strong reactivators of acetylcholinesterase enzymes and play an important role as dephosphorylating agent toward the organophosphate esters.[4] A promising strategy incorporates the removal of phosphoryl moiety from the active site of AChE and restores the activity of enzyme. Functionalized surfactants are among the most powerful and efficient reagents for the detoxification of organophosphorus pesticides because of their high solubilizing power[5–8] and high polarity, but pesticides are compounds of low polarity and their chemical decontamination is less effective in aqueous media.[9,10] The investigation of the α-nucleophiles for the detoxification of organophosphorus pesticides has received major attention due to their superior reactivity as compared to normal nucleophiles. Oximes because of their α-effect nucleophilic reactivity and a proficient approach to weaken toxicity are used as antidotes for the reactivation of organophosphorus pesticides.[11,12] Phosphate esters, for the most part mono- and diesters, are ever-present in nature and are fundamental segments of coenzymes, hereditary materials, vitality repositories, and so on. Because of the biological consequence of these esters, their ecological evidences and degradation have been broadly examined over the previous decades.[13–17]

Over the past several years, efforts have been made to develop a huge number of mono- and bispyridinium oximes, which are a vital group of medications utilized as a remedy for the treatment of profoundly harmful organophosphorus compounds.[18–20] Voicu and his group[21] designed some oximes reactivators to enhance BBB (blood brain barrier)



SCHEME 1 Reaction of phosphate esters with oximes in micellar media [Color figure can be viewed at wileyonlinelibrary.com]

penetration. Recently, Ghosh and co-workers[22] present an excellent article, which describes the design and synthesis of different metallosurfactant aggregates as catalysts for the hydrolysis of carboxylate and phosphate esters. Toullec and Moukawim[23] reported cetyltrimethylamrnonium hydroperoxide as an efficient reagent for promoting phosphate ester hydrolysis. Simanenko and co-workers[24] synthesized imidazolium halides, which are functionalized zwitterionic surfactants and give rise to micelle formation. Biresaw and Bunton[25] described a stepwise self-association model and observed that bimolecular rates in water and "organized assemblies" are usually similar, where "catalysis" by micelles and other organized assemblies are due to the concentration effect. Similarly, Hampl et al.[26] discussed how structure and lipophilicity of functionalized surfactants influence their reactivity in micelles and microemulsion. They proved that the lipophilicity is the most important factor influencing the localization and reactivity of functionalized surfactants in nanoaggregates. Cuccovia and co-workers[27] determined the effects of micelles and vesicles on the rate of oximolysis of *p*-nitrophenyldiphenyl phosphate and a model system for surfactant-based skin defensive formulations against organophosphates. Here, we have investigated the acid dissociation constant (pK_a) and hydrolytic efficacy of oximes and oxime-functionalized pyridinium surfactant 4- hydroxyiminomethyl-1-alkylpyridinium bromide (alkyl chain length dodecyl, 4-C_{12} and decyl, 4-C_{10}) toward the cleavage of phosphate (paraoxon) and thiophosphate (parathion and fenitrothion) esters in the presence of cationic surfactants cetyltrimethylammonium bromide (CTAB) and cetylpyridinium bromide (CPB) (Scheme 1).

2 | MATERIALS AND METHODS

2.1 | Materials

Paraoxon, parathion, CTAB, CPB, 4-pyridinealdoxime (4-PyOx), and 2-pyridinealdoxime (2-PyOx) were obtained from Sigma/Aldrich (Bangalore, India). Quaternized oxime, 4-hydroxyiminomethyl-1-alkyl pyridinium bromide (alkyl = C_nH_{2n+1} n = 10, 12), was prepared according to the literature method.[28] Water used for the preparation of samples was deionized and triply distilled.

2.2 | Methods

2.2.1 | Determination of acid dissociation constant (pK_a)

The acid dissociation constants (pK_a) values of all the different oxime-based functionalized surfactant 4-(hydroxyimino) methyl)-1-alkylpyridinium bromide ions (alkyl = 4-C_{10}PyOx$^-$, 4-C_{12}PyOx$^-$, 4-C_{14}PyOx$^-$, 4-C_{16}PyOx$^-$) were determined by potentiometric, kinetic, and spectrophotometric methods.

2.2.2 | Potentiometric method

The acidity constant (pK_a) values of oximes were calculated at 27°C by the potentiometric titration method using an Orion Star A-211 pH-meter (Figure 1). All functionalized oximes were titrated with 0.01 M NaOH, and the ionic strength was maintained constant at 0.1 M by adding KCl. The pK_a values

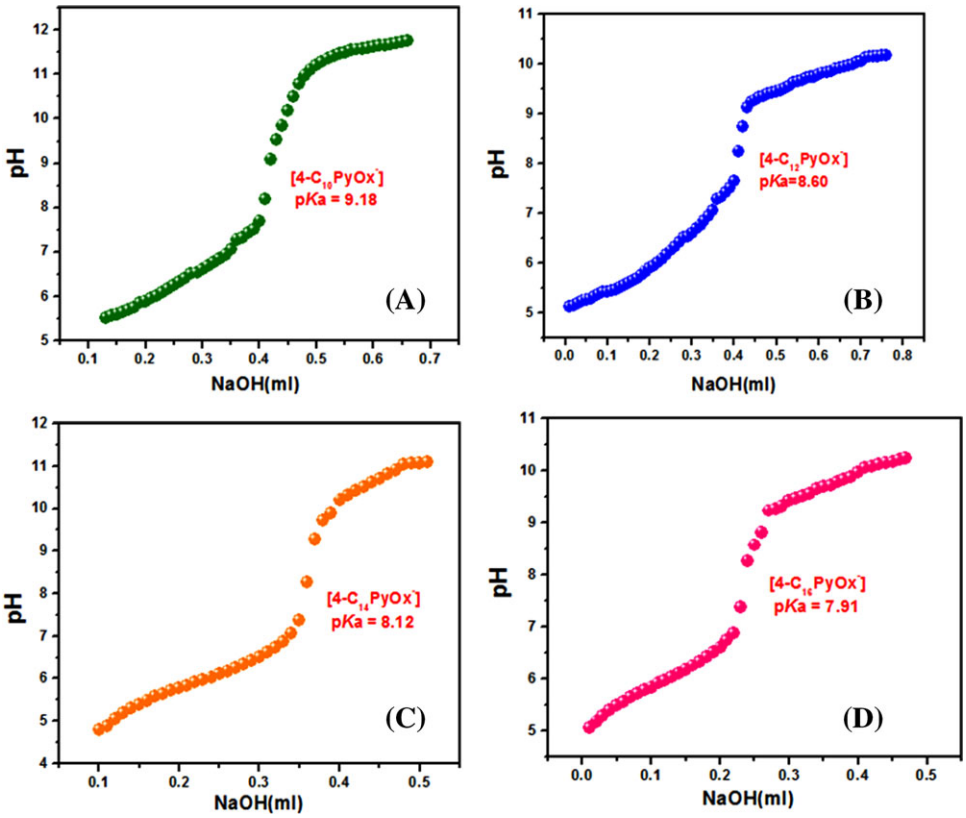


FIGURE 1 Determination of acid dissociation constant (pK_a) of (A) 4-C_{10}PyOx$^-$, (B) 4-C_{12}PyOx$^-$, (C) 4-C_{14}PyOx$^-$, and (D) 4-C_{16}PyOx$^-$ [Color figure can be viewed at wileyonlinelibrary.com]

were calculated by means of Equation 1 from the measured pH values of the solution:

$$pK_a = \text{pH} - \log \frac{[A^-]}{[HA]} \quad (1)$$

2.2.3 | Spectrophotometric method

The pK_a values of all the functionalized oximes were determined spectrophotometricaly using a Thermofisher Evolution 300 UV-Visible spectrophotometer equipped with a temperature controller (Peltier) by using a well-known method of Albert and Sergeant.[29] It is based on direct determination of the ratio of protonated to deprotonated species in buffer solutions. An aliquot (3 mL) of a stock solution (5×10^{-4} M) of functionalized oxime in triple-distilled water was diluted with a 25-mL phosphate buffer solution. The absorption spectrum was recorded in the range of 200–600 nm and at different pH values. Different pH values ranging from 6.01 to 10.50 were maintained using different compositions of phosphate buffer. After each pH adjustment, the solutions were transferred into the cuvette and the absorption spectra were recorded. The average values of 10 measurements were considered as the pK_a of the compound with respect to oxime functionality. The calculations of pK_a were made around half neutralization using the following equation:

$$pK_a = \text{pH}_{exp} - \log \frac{\text{Abs}_\psi - \text{Abs}_{H_{ox}}}{\text{Abs}_{ox} - \text{Abs}_\psi} \quad (2)$$

where Abs_{HOx} is the absorbance of the unionized form of oxime, Abs_ψ is the absorbance of the partially ionized form of oxime, and Abs_{Ox} is the absorbance of fully ionized form of oxime. The absorbance at 340 nm for [4-C_{10}PyOx$^-$] was plotted against the pH of the buffer solutions. The sigmoidal curves (Figure 2) were obtained, and pK_a values were calculated based on their determinations around the point of half neutralization using Equation 2. pK_a values of functionalized oxime (4-hydroxyiminomethyl-1-alkylpyridinium bromide) are presented in Table 1, which are quite well in agreement with the literature values.[30] The spectrophotometric determination of pK_a of oxime [4-C_{10}PyOx$^-$] is shown in Figure 3.

2.2.4 | Kinetic method

The apparent pK_a values of some oxime-based functionalized nucleophiles have been determined by measuring the first-order rate constant for the hydrolysis of paraoxon at different pH values (6–10) in the presence of functionalized oximes.

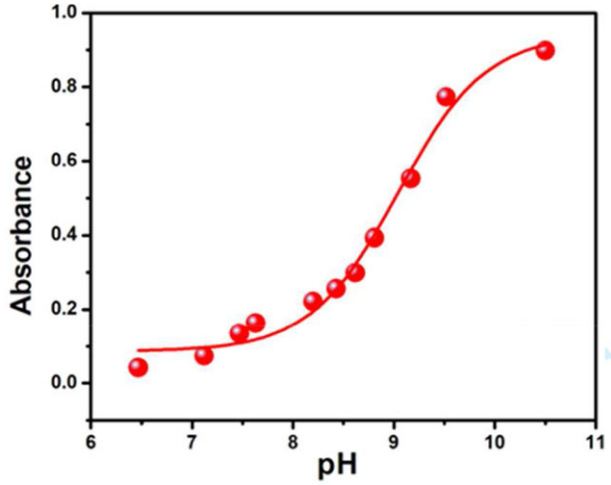


FIGURE 2 Plot between absorbance (340 nm) and pH for 4-hydroxyiminomethyl-1-decylpyridinium bromide [4-C_{10}PyOx$^-$] [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Acid dissociation constants (pK_a) of functionalized surfactants (4-hydroxyiminomethyl-1-alkyl pyridiniumbromide) with alkyl chain lengths (C_{10}, C_{12}, C_{14}, C_{16}) determined by kinetic, potentiometric, and spectrophotometric methods

	pK_a		
Functionalized surfactant	**Kinetic method**	**Potentiometric method**	**Spectrophotometric method**
4-C_{10}PyOx	9.20	9.18	9.34
4-C_{12}PyOx	8.71	8.60	9.18
4-C_{14}PyOx	8.16	8.12	8.55
4-C_{16}PyOx	_	7.91	8.32

The data indicate that the rate of reaction increases with an increase in pH values. Figure 4 shows the plots of log k_{obs} versus pH at different pH values. The pK_a values obtained by the kinetic method agreed well with those measured by the spectrophotometeric and conductometric methods (Table 1).

2.3 | Kinetic treatment

The pseudo–first-order rate constants for the hydrolysis of phosphate esters in the presence of oxime-based functionalized surfactants were determined at 27°C by monitoring the formation of the *p*-nitrophenoxide anion at wavelength 400 nm using a Thermofisher Evolution 300 UV–visible spectrophotometer equipped with a temperature controller (Peltier). Rate constants for the cleavage of phosphate esters by oximes were determined at an ionic strength of 0.1 M KCl. Borate buffer was employed to control the pH of the reaction media. All reactions were conducted under pseudo–first–order conditions. The pseudo–first-order rate constants (k_{obs}) were determined by the least-squares fit method. The intercept were negligible. Figure 5 shows the UV–visible

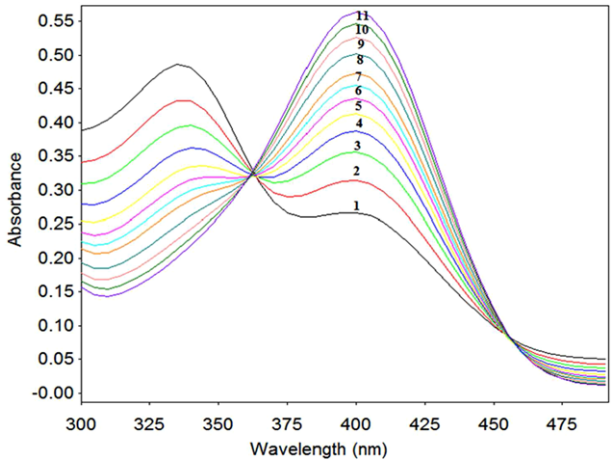


FIGURE 3 Spectrophotometric determination of pK_a of oxime [4-C_{10}PyOx$^-$] of oxime [Color figure can be viewed at wileyonlinelibrary.com]

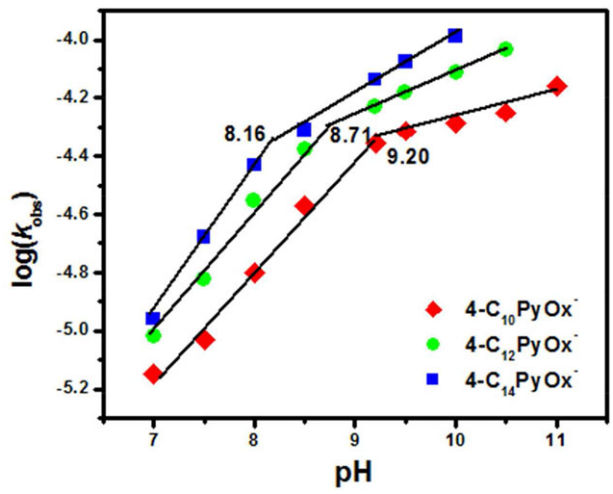


FIGURE 4 Plots of log k_{obs} versus pH for the cleavage of paraoxon in the presence of 4 hydroxyiminomethyl-1-alkylpyridinium bromide (C_{10} and C_{12} and C_{14}). Reaction conditions: [paraoxon] = 1×10^{-4} M, [4-C_n] = 1×10^{-3} M, [KCl] = 0.1 M, [CTAB] = 1.0 mM, temperature = 27°C [Color figure can be viewed at wileyonlinelibrary.com]

spectra at 400 nm with an increase in absorbance of the *p*-nitrophenoxide ion for the hydrolysis of paraoxon with 4-C_{10}PyOx at 1.0 mM CTAB.

3 | RESULTS AND DISCUSSION

The effects of pH, nucleophile, and surfactants were evaluated on the kinetic behavior of pyridinium-based functionalized surfactants. It can be noted that a pyridinium surfactant is an efficient supernucleophile for the cleavage of various phosphate esters in micellar medium. The study aimed at cleavage of phosphate esters (paraoxon,

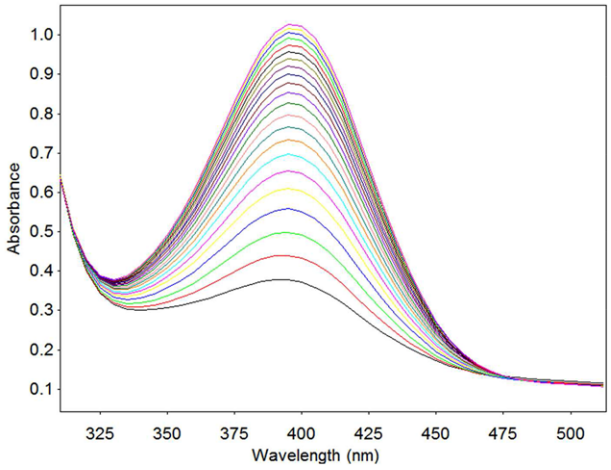
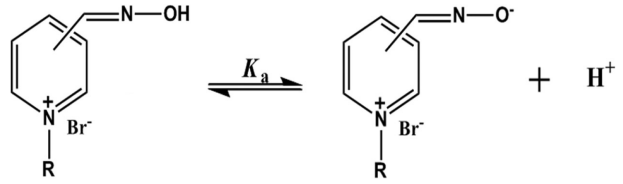


FIGURE 5 UV–visible spectra for the cleavage of paraoxon with 4-C_{10}PyOx$^-$ in cationic micellar media at different reaction times. Reaction conditions: [Paraoxon] = 1×10^{-4} M, [Nu$^-$] = 1×10^{-3} M, [KCl] = 0.1 M, borate buffer pH 9.2, [CTAB] = 1.0 mM, temperature = 27°C [Color figure can be viewed at wileyonlinelibrary.com]

parathion, and fenitrothion) with pyridinium-functionalized surfactants. The rate constants for the hydrolysis of phosphate esters (paraoxon, parathion, and fenitrothion) by oximate (2-PyOx$^-$ and 4-PyOx$^-$) and functionalized oximate, 4-hydroxyimminomethyl 1-alkyl pyridinium bromide, were determined at 27°C in the presence of CTAB by employing different buffers (phosphate and borate) ranging from pH 7 to 11 as added to the reaction medium. The pH-dependent rate constants increase with increasing pH (7–12) in the presence of cationic surfactant CTAB, which is shown in Figure 6. Consequently, the oxime group dissociates and forms the oximate ion, which acts as an α- nucleophile and shows drastic change at pH > pK_a [Ref. 31] and hence proved that 4-C_{14}PyOx$^-$ + CTAB to be the most efficient system for ester cleavage because of its lower pKa (8.16), which plays a significant role in the hydrolysis of phosphate ester (Scheme 2).



SCHEME 2 Deprotonation of pyridinium oxime

The ionized form of oxime (−CH=NOH), i.e., the oximate ion (−CH=NO$^-$), plays a significant role in the cleavage of phosphate esters. The data on the effect of pH on the hydrolysis of paraoxon, parathion, and fenitrothion with oximate and its functionalized oximate (4-C_nPyOx$^-$) in the presence of CTAB micelles are presented in Tables S1–S3 in the Supporting Information. Under comparable conditions, oximate ions showed the highest reactivity toward paraoxon as compared to other substrates due to the difference in electrophilic centers from carbonyl to sulfonyl or phosphonyl group (P=O and P=S). As shown in the data obtained in Table 2, paraoxon (P=O) with high electrophilicity shows more reactivity than fenitrothion (S=O) with low electrophilicity because of the poorer electron-donating ability of thioanion in ejecting the leaving group as compared to oxyanion. Also, the electrophilicity of the central atom P of P=O center diminishes, which hinders the attack of α-nucleophile in the rate-determining step.[32]

To determine the efficiency of oximes and functionalized oximes, the rate of hydrolysis of phosphate esters on the first-order rate constants has been studied in various concentrations of different alkyl chain lengths (C_{10}–C_{14}) in CTAB at pH 9.5. The results are summarized in Tables S4–S6 in the Supporting Information. Variation in the surfactant chain length has a substantial effect on k_{obs} values for the reaction of phosphate esters (Table 3 and Figure 7). For the hydrolysis of phosphate esters, 4-C_{14} was found to be the most reactive system and the rate constants increase with an increase in the

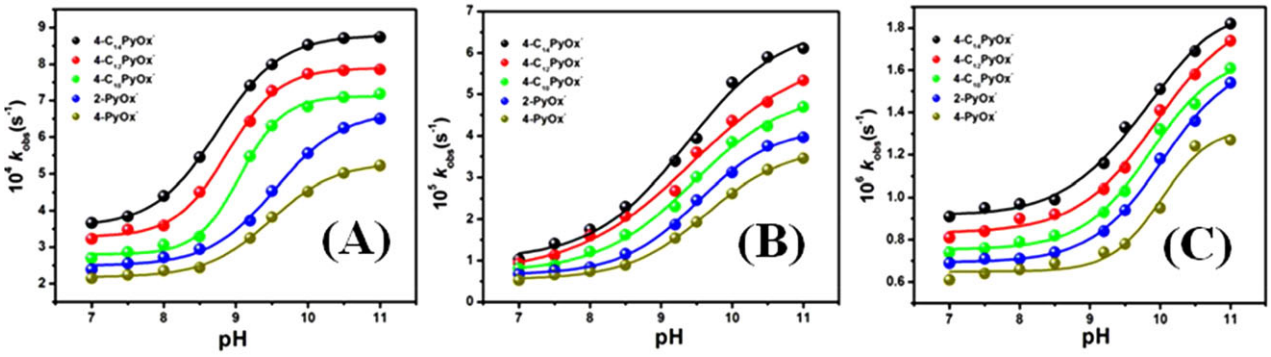


FIGURE 6 pH rate profiles for the reaction of oximate and functionalized oximate ions with (A) paraoxon, (B) parathion, and (C) fenitrothion. Reaction conditions: [substrate] = 1×10^{-4} M, [Nu$^-$] = 1×10^{-3} M, [CTAB] = 1.0 mM, μ = 0.1 M KCl, pH 9.5, temperature = 27°C [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Kinetic rate data for the reaction of phosphate esters with oximate and functionalized oximate ions in the presence of cationic surfactants [CTAB]

	$10^4\ k_{obs}\ (s^{-1})$				
Substrate	**4-C_{14}PyOx$^-$**	**4-C_{12}PyOx$^-$**	**4-C_{10}PyOx$^-$**	**2-PyOx$^-$**	**4-PyOx$^-$**
Paraoxon	7.44	6.41	5.42	3.69	3.19
Parathion	0.28	0.24	0.22	0.18	0.15
Fenitrothion	0.08	0.08	0.09	0.01	0.02

Reaction conditions: [Substrate] = 1×10^{-4} M, [Nu$^-$] = 1×10^{-3} M, [CTAB] = 1.0 mM, μ = 0.1 M KCl, pH 9.2, temperature = 27°C.

TABLE 3 Effect of alkyl chain length for the hydrolysis of phosphate esters

	Paraoxon		**Parathion**		**Fenitrothion**	
	$10^4\ k_{obs}\ (s^{-1})$		$10^5\ k_{obs}\ (s^{-1})$		$10^6\ k_{obs}\ (s^{-1})$	
[Nu$^-$] (mM)	**4-C_{12}PyOx$^-$**	**4-C_{10}PyOx$^-$**	**4-C_{12}PyOx$^-$**	**4-C_{10}PyOx$^-$**	**4-C_{12}PyOx$^-$**	**4-C_{10}PyOx$^-$**
0.0	0.85	0.85	0.62	0.62	0.45	0.45
0.5	4.21	3.34	1.65	1.39	0.71	0.74
0.8	5.55	4.34	2.23	1.95	0.82	0.88
1.0	6.41	5.42	2.48	2.29	0.89	0.95
2.0	8.21	7.12	3.44	2.97	1.12	1.22
3.0	8.44	8.22	4.02	3.54	1.23	1.35
4.0	8.79	8.38	4.32	3.91	1.32	1.42

Reaction conditions: [substrate] = 1×10^{-4} M, [Nu$^-$] = 1×10^{-3} M, [CTAB] = 1.0 mM, μ = 0.1 M KCl, pH 9.5, temperature = 27°C.

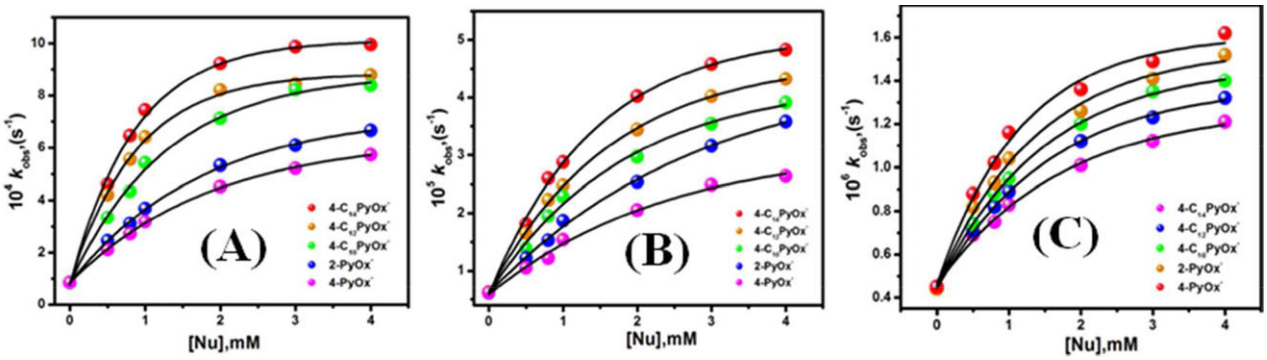


FIGURE 7 Rate surfactant concentration profile for the reaction of oximate and functionalized oximate ions in (A) paraoxon, (B) parathion, and (C) fenitrothion. Reaction conditions: [substrate] = 1×10^{-4} M, [Nu$^-$] = 1×10^{-3} M, [CTAB] = 1.0 mM, μ = 0.1 M KCl, pH 9.5, temperature = 27°C [Color figure can be viewed at wileyonlinelibrary.com]

alkyl chain length of functionalized surfactants in the following order: 4-C_{14} > 4-C_{12} > 4-C_{10}. It is mainly explained on the basis of hydrophobicity, electrical surface potential of the micelle, and also due to steric hindrance. 4-C_{14} possesses the least steric hindrance and due to this reason it shows higher reactivity.[33]

There have been a large number of reports on the effect of surfactant on the rate of ester cleavage by using various substrates and oximes. The cleavage of phosphate esters with oximate ions in the presence of cationic surfactants CTAB and CPB at pH 9.5 is clearly manifested in Figures 8 and 9 and in Tables S7 and S8 in the Supporting Information. The k_{obs} values for the reactions in the micellar system are evaluated through k_{obs} versus surfactant concentration profiles. It can be observed that with an increase in the concentration of surfactants the reaction rate also increases at a fixed concentration of nucleophile because of the transfer of nucleophile into the micellar pseudophase and then decreases with further addition of the surfactants due to the dilution of nucleophile at micellar-catalyzed reactions.[34] It is well known that the micelles bring reactants closer because of electrostatic attraction of the nucleophile and hydrophobically binding of the substrate. The extent of micellar catalysis is expected to be depending on the relative amount of substrate incorporated in micelles.

By comparing the head group of various surfactants, the rate constants were found to be higher with a surfactant having an aromatic group, that is CPB has more catalytic activity as compared to CTAB. The order of reactivity is in the following order: CPB > CTAB. that is the surfactant having a

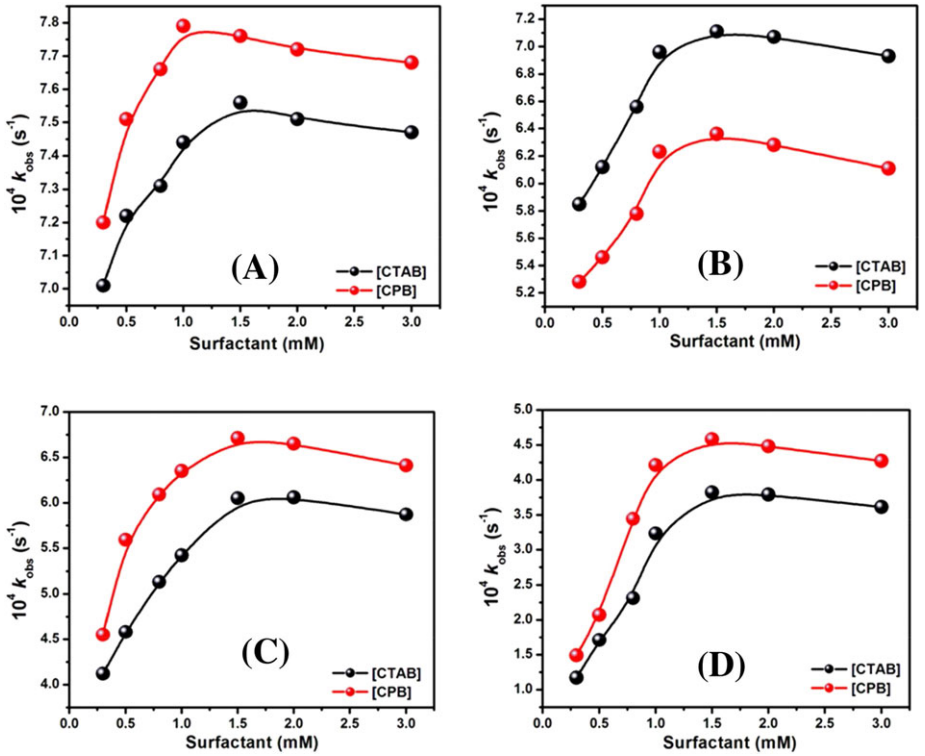


FIGURE 8 Effect of surfactants on reaction of paraoxon with (A) 4-C_{14}PyOx$^-$, (B) 4-C_{12}PyOx$^-$, (C) 4-C_{10}PyOx$^-$, and (D) 4-PyOx$^-$ in the presence of cationic surfactant. Reaction conditions: [paraoxon] = 1.0×10^{-4} M, [Ox$^-$] = 1.0×10^{-3} M, pH 9.5, μ = 0.1 M KCl, temperature = 27°C [Color figure can be viewed at wileyonlinelibrary.com]

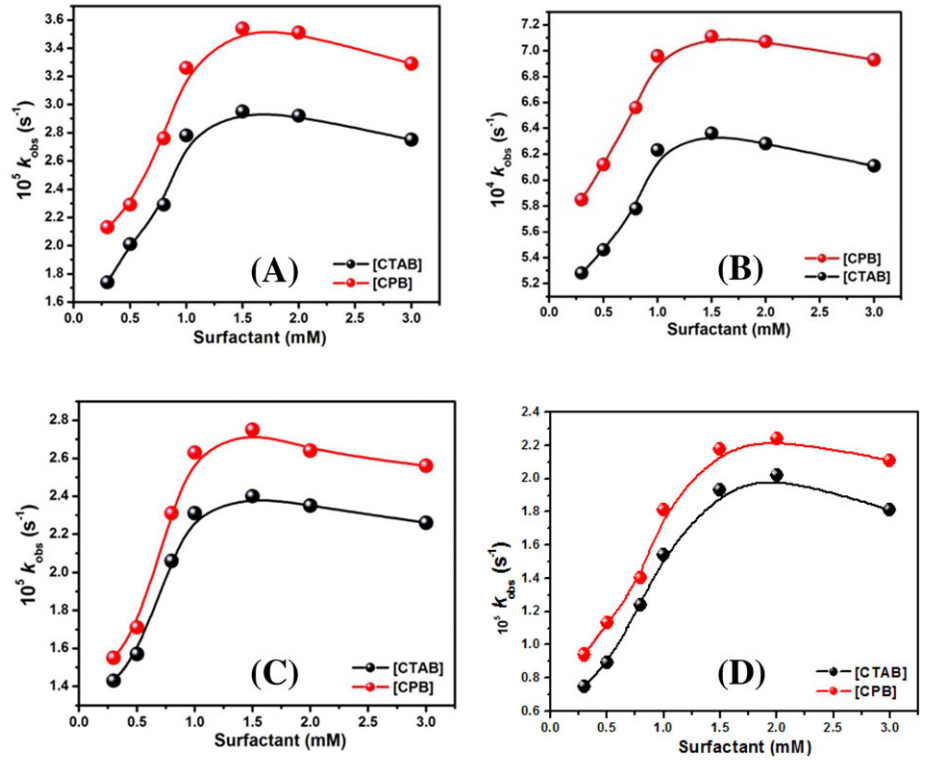


FIGURE 9 Effect of surfactants on reaction of parathion with (A) 4-C_{14}PyOx$^-$, (B) 4-C_{12}PyOx$^-$, (C) 4-C_{10}PyOx$^-$, and (D) 4-PyOx$^-$ in the presence of cationic surfactant. Reaction conditions: [parathion] = 1.0×10^{-4} M, [Ox$^-$] = 1.0×10^{-3} M, pH 9.5, μ = 0.1 M KCl, temperature = 27°C [Color figure can be viewed at wileyonlinelibrary.com]

bulky head group and with the aromatic ring showed higher reactivity than alkyl ammonium head groups.

4 | CONCLUSIONS

In the present investigation, an attempt has been made to investigate the kinetic efficiency of pyridinium-based functionalized surfactants toward the micellar hydrolysis of phosphate esters. Considerable enhancement in the rate of hydrolysis reaction was observed on increment of the alkyl chain length of functionalized surfactants. 4-C_{14}PyOx^{-}/CPB was found to be the most reactive system among all the investigated oximes for the cleavage of phosphate esters. These systems are very efficient in promoting phosphate esterolysis. Results of the present investigation provide useful information for development of an effective system for degradation of toxic pesticides and nerve agents.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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