Research Article

Journal of Physical Organic Chemistry

Received: 15 July 2009, Revised: 8 September 2009, Accepted: 22 September 2009, Published online in Wiley InterScience: 4 January 2010

(www.interscience.wiley.com) DOI 10.1002/poc.1635

# Functionalized surfactant mediated reactions of carboxylate, phosphate and sulphonate esters

**Shuchi Tiwari[a], Kallol K. Ghosh[a]*, Jan Marek[b] and Kamil Kuca[b]**

**Nucleophilic reactivity of some functionalized surfactants, i.e. quaternary pyridinium aldoximes towards the hydrolysis of *p*-nitrophenyl acetate (PNPA), *p*-nitrophenyl benzoate (PNPB), *p*-nitrophenyldiphenyl phosphate (PNPDPP) and *p*-nitrophenyl *p*-toluene sulphonate (PNPTS) has been studied at pH 7.1 and 27 °C. Addition of functionalized surfactant to reaction medium causes progressive increase in the rate of hydrolysis and reaches a maximum and then decreases due to further addition of surfactant. An increase in the alkyl chain length of functionalized surfactants resulted in an increase in the first-order rate constant. The apparent p$K_a$ and CMC of functionalized surfactants have also been determined by spectrophotometric and conductometric methods, respectively. Copyright © 2010 John Wiley & Sons, Ltd.**

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

**Keywords:** functionalized surfactants; kinetics; micelles; pyridinium aldoximes

## INTRODUCTION

Currently, there is tremendous excitement and sustained research efforts in the study of detection, sensing and decontamination of chemical and biological warfare agents.[1–6] Organophosphorus compounds are widely used as pesticides and chemical warfare nerve agents and they exhibit significant toxicity towards mammalian organisms. Acetylcholine is required for the transmission of nerve impulses in the brain, skeletal muscles and other areas. However, after the transmission of the impulse, the acetylcholine must be hydrolyzed to avoid over stimulating or overwhelming the nervous system. This breakdown of the acetylcholine is catalyzed by an enzyme called acetylcholinesterase (AChE; EC 3.1.1.7).[7–12] The intoxification with nerve agents leads to the inhibition of AChE by phosphorylation of their active site serine residue. Therefore, the search for reactivators of acetylcholinesterase and novel catalysts capable of detoxifying chemical warfare agents and pesticides is still a challenge and an ongoing priority for research.

Different types of $\alpha$-nucleophiles, metallosurfactants and functionalized surfactants have been designed as potential hydrolytic micellar catalysts.[13–23] The recent research has been focused primarily on the reactive functional group incorporated into the micelle forming molecules. However, the influence of the relative position of polar head group, hydrophobic alkyl chain length and nucleophilic function on the hydrolytic efficiency of functionalized surfactants has not been explored properly.[20–23] Epstein *et al.*[24] used hydroximinomethyl pyridinium type surfactants for the hydrolysis of organophosphates. Similarly Hampl and co-workers[25] synthesized several amphiphilic quaternary pyridinium ketoximes and examined their efficiency in the hydrolysis of *p*-nitrophenyldiphenyl phosphate. Simanenko *et al.*[26] performed a detailed kinetic analysis of nucleophilic cleavage of some phosphate and sulphur esters in the presence of new functionalized surfactants whose head part includes a ring and hydroxyimino group. Recently, Cuccovia *et al.*[27] used 1-dodecyl-2-(hydroxyimino) methyl pyridinium chloride for the oximolysis of *p*-nitrophenyldiphenyl phosphate.

For the last few years, we have been interested in the study of catalytic efficiency of different $\alpha$-nucleophiles for the hydrolysis of carboxylate and phosphate esters in self-organized systems.[28–35] In continuation of these investigations, we herein examined the comparative hydrolytic efficiency of oxime-based functionalized surfactants, i.e. 3-hydroxyiminomethyl-1-alkylpyridinium bromide series (IA) (Scheme 1) for the different esters.

In addition to 3-substituted aldoximes, an attempt has also been made to use some 4-substituted aldoximes (IB) series ($C_8H_{17}$, $C_{10}H_{21}$). The apparent p$K_a$ and CMC of functionalized surfactants have also been determined by spectrophotometric and conductometric methods, respectively.

## RESULTS AND DISCUSSION

Hydrolytic cleavage of all the esters was evaluated by measuring the kinetics of the hydrolysis of model substrates using functionalized surfactants. The reaction rate increased with rise

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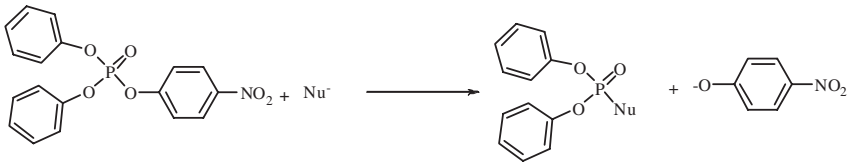
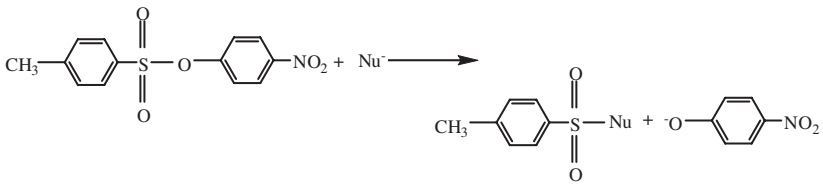
R = $CH_3$, *p*-nitrophenyl acetate (PNPA)

R= $C_6H_5$, *p*-nitrophenyl benzoate (PNPB)

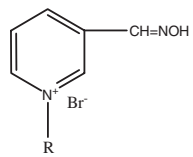


*p*-nitrophenyldiphenyl phosphate (PNPDPP)



*p*-nitrophenyl *p*-toluene sulphonate (PNPTS)

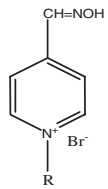
**$Nu^-$**



(IA)

3-hydroxyiminomethyl -1-alkyl pyridinium bromide

(R= $C_8H_{17}$, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$)



(IB)

4-hydroxyiminomethyl -1- alkyl pyridinium bromide

(R= $C_8H_{17}$, $C_{10}H_{21}$)

**Scheme 1.**

in both nucleophile concentration and pH (Table S1, supporting information). Neglecting in a first approximation the contribution of hydroxide ion as well as of water to the hydrolysis process at pH 7.1, the expected reaction rate law may be expressed as

$$\text{Rate} = k[\text{Ox}^-][\text{Ester}]$$

The nucleophilic centre is located in the oximates moiety. As the functionalized surfactant concentration increased the reaction rate considerably increased. When the substrate is completely bound with micelles, the reaction rate no longer depends on the surfactant concentration, and $k_{obs}$ tends to maximum. Subsequent addition of functionalized surfactant causes a decrease in the observed reaction rate. This may be due to the dilution of the catalyst in the Stern layer of micelles. An advantage of such surfactants is that the role of nucleophilic reagents is played just by the functionalized surfactant which gives rise to micelle formation. Structures of pyridinium detergents with oxime group as nucleophilic function able to split nerve agents were designed from the pralidoxime structure. Pralidoxime, monoquaternary pyridinium aldoxime, is known to be a good nuclephile used as an antidote in the case of nerve agent intoxication. Its antidotal effect is based on the splitting of the covalent bond between enzyme acetylcholinesterase and nerve agent. Owing to this, the design of pralidoxime-like detergents seemed to be good approach of how to improve the potency of the quaternary detergent to hydrolyze nerve agents. Amphiphilic quaternary pyridinium aldoximes and ketoximes show highest reactivity. The source of the observed reactivity of these catalysts can be explained by using electronic effect in the pyridium ring. The electron-withdrawing effect of the quaternary nitrogen in pyridinium oximes increases the acidity of the hydroxyimino group which is relatively low in non-substituted aromatic or aliphatic oximes ($pK_a \approx 12$–13). The increased acidity of the pyridinium aldoximes and ketoximes ($pK_a \approx 8$–10) provides sufficient concentration of the nucleophilic oximate anion even in neutral solutions. Thus, the oxime-based functionalized surfactants are considerably reactive towards organophosphates under mild conditions. All these functionalized surfactants are superior to normal $\alpha$-nucleophiles. Micelles formed by zwitterionic species whose head part includes a covalently linked typical $\alpha$-nucleophile group can be regarded as a unique super-nucleophilic system

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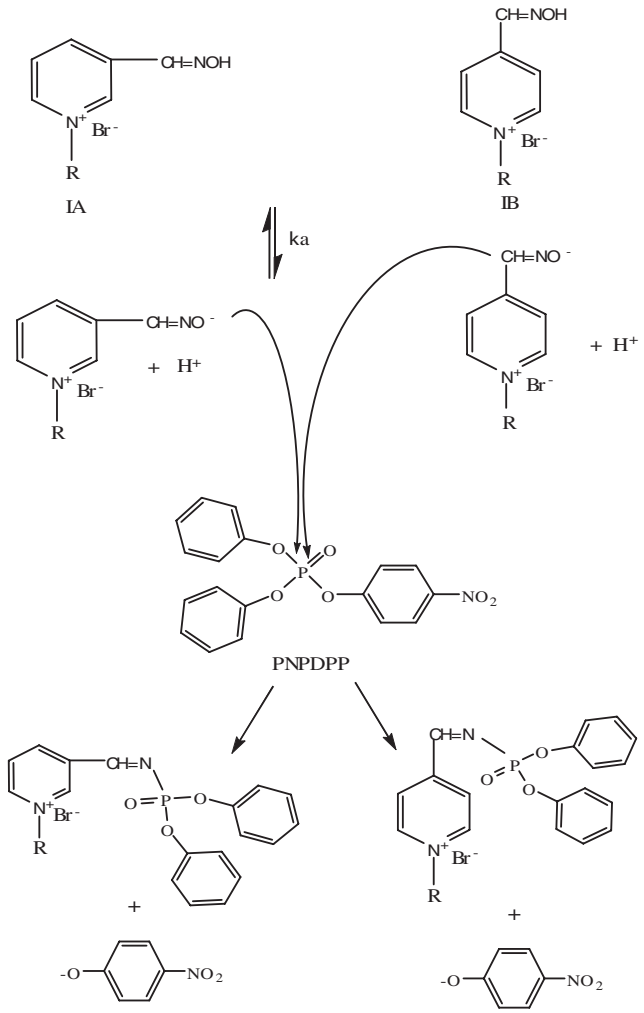



**Scheme 2.**

ensuring high rates of substrate cleavage due to reactant concentration effect. The representative mechanism for phosphate ester is given in Scheme 2.

### Effects of alkyl chain length

The effect of the functionalized surfactants with different alkyl chain lengths ($C_8$–$C_{16}$) on the hydrolysis of carboxylate, phosphate and sulphur esters was also determined. Variation in the surfactant chain length has a significant effect on $k_{obs}$ values for the reaction of PNPA (Fig. 1). The $k_{obs}$ values increase with increase in the alkyl chain length of the surfactants (Figs 1 and 2). This increase in the order is mainly due to the increase in the electrical surface potential of the micelle in the above order and also due to an increase in the hydrophobicity of the palisade layer of micelle in the above order. The rate maximum depends upon CMC of the functionalized surfactants. The increase in the chain length of the surfactant causes a decrease in CMC. The formation of micelles is affected by both the hydrophobicity of the surfactant and the polarity of the bulk solution. The relative hydrophobicity of the surfactants increases with chain length, resulting in the thermodynamic threshold required for the formation of micelles to be reached at lower surfactant concentrations with longer chain length surfactants. The high

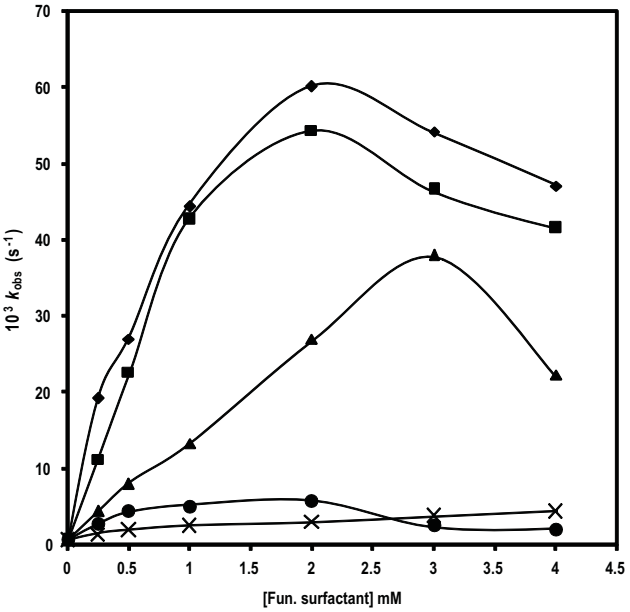



**Figure 1.** Plots for the reaction of *p*-nitrophenyl acetate (PNPA) with different oxime-based (series 3) functionalized surfactants. $C_{16}$-(◆), $C_{14}$-(■), $C_{12}$-(▲), $C_{10}$-(●) and $C_8$-(x). This figure is available in colour online at www.interscience.wiley.com/journal/poc

reactivity of the oximates ion with carboxylate and organophosphorus esters is well documented.[36–38]

### Comparative reactivity of series (IA and IB) functionalized surfactants

In order to compare the reactivity of IA and IB series, the rate of hydrolysis of PNPA, PNPB and PNPDPP has been studied in

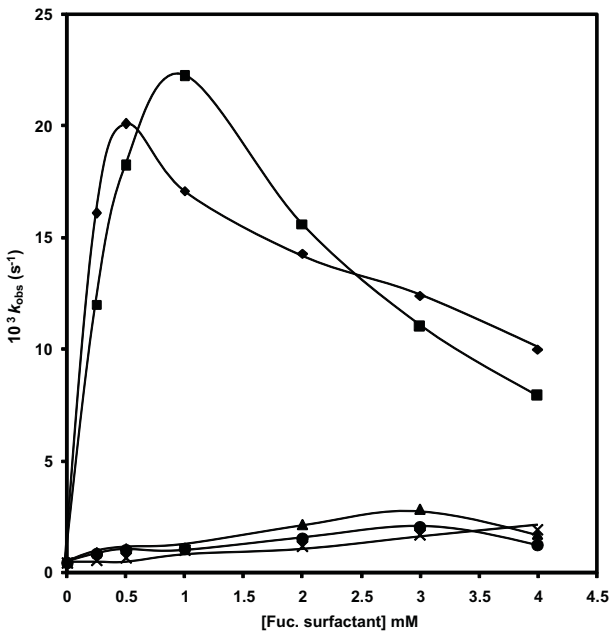



**Figure 2.** Plots for the reaction of *p*-nitrophenyldiphenyl phosphate (PNPDPP) with different oxime-based (series 3) functionalized surfactants. $C_{16}$-(◆), $C_{14}$-(■), $C_{12}$-(▲), $C_{10}$-(●) and $C_8$-(x). This figure is available in colour online at www.interscience.wiley.com/journal/poc



**Table 1.** First-order rate constants for the hydrolysis of different substrates (PNPA, PNPB, PNPDPP) in the presence of functionalized surfactants of (IA and IB) series

| | $10^3\ k_{obs}(s^{-1})$ | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | PNPA | | | | PNPB | | | | PNPDPP | | | |
| | IA | | IB | | IA | | IB | | IA | | IB | |
| [Functionalized surfactant] mM | ($C_8$) | ($C_{10}$) | ($C_8$) | ($C_{10}$) | ($C_8$) | ($C_{10}$) | ($C_8$) | ($C_{10}$) | ($C_8$) | ($C_{10}$) | ($C_8$) | ($C_{10}$) |
| 0.0 | 0.59 | 0.59 | 0.59 | 0.59 | 0.58 | 0.58 | 0.58 | 0.58 | 0.45 | 0.45 | 0.45 | 0.45 |
| 0.25 | 1.25 | 2.72 | 0.63 | 0.90 | 0.98 | 1.55 | 0.59 | 0.72 | 0.54 | 0.85 | 0.46 | 0.57 |
| 0.50 | 1.91 | 4.50 | 1.00 | 1.56 | 1.50 | 2.13 | 0.75 | 1.00 | 0.67 | 0.99 | 0.48 | 0.69 |
| 1.0 | 2.44 | 5.05 | 1.87 | 2.98 | 2.21 | 2.82 | 0.95 | 1.86 | 0.98 | 1.04 | 0.49 | 0.87 |
| 2.0 | 2.93 | 5.71 | 3.81 | 5.25 | 1.90 | 3.51 | 1.40 | 3.67 | 1.16 | 1.51 | 0.88 | 1.17 |
| 3.0 | 3.76 | 2.45 | 6.52 | 8.61 | 1.32 | 2.62 | 1.83 | 2.78 | 1.69 | 2.03 | 1.75 | 1.40 |
| 4.0 | 4.37 | 2.06 | 7.15 | 10.5 | 0.99 | 1.92 | 2.81 | 2.25 | 1.92 | 1.25 | 2.00 | 1.05 |

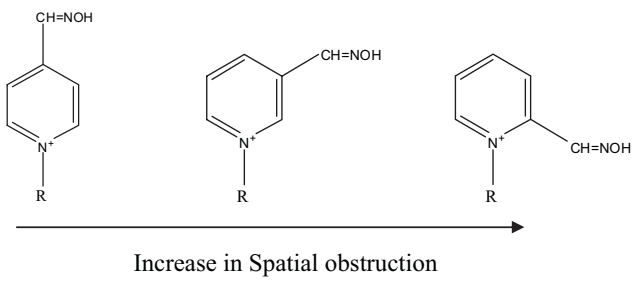
Temp. = 27 °C, [Substrate] = $0.5 \times 10^{-4}$ M, $\mu$ = 0.1 M KCl, pH = 7.1.

functionalized surfactants having $C_8$ and $C_{10}$ alkyl chain lengths. Studies could not be made for 4-substituted pyridinium aldoximes functionalized surfactants having $C_{12}$, $C_{14}$, $C_{16}$ alkyl chain lengths due to solubility problem and turbidity in reaction medium.

It is evident from the rate data shown in Table 1 that IB functionalized surfactant $C_8$ and $C_{10}$ are more reactive compared to IA functionalized surfactants. It may be due to the low critical micelle concentration (CMC) of IB functionalized surfactants compared to IA functionalized surfactants. Therefore, they can be capable of providing the kinetic benefit of micellar catalysis even at low concentration.

According to Kuca *et al.*[39] there exists some relationship between the position of the oximate group and the ability to reactivate AChE, inhibited by different kinds of nerve agents. Position of the oxime group influences the spatial properties of the reactivators. Spatial obstruction increases from 4 to 2 positions (Scheme 3). Therefore, reactivators having the oxime group at position −4 are more reactive.

The reactivity difference of IA and IB series can also be explained on the basis of electronic effect, since the acidity of oximes IB ($pK_a = 8.1$) is higher than that of the oxime IA ($pK_a = 9.2$). Lower $pK_a$ value of IB series surfactants increases the electron withdrawing effect of the quaternary nitrogen in the pyridinium ring of these surfactants. Therefore, they provide sufficient concentration of nucleophilic oximate anion which is responsible for the higher reactivity of IB series compared to IA series.




**Scheme 3.**

### Comparative study of efficacy of functionalized surfactants towards different electrophilic centres

According to the data presented in Table 1 (and in Tables S2–S5 in the supporting information), deprotonated hydroxyl imino anion (released from series (IA) functionalized surfactants) shows variation in its efficiency towards different electrophilic centres (C═O, P═O and S═O). Changing the electrophilic centre from a carbonyl to a sulphonyl or phosphonyl group would exert significant effect on their electrophilicity. Its reactivity order for all the substrates are PNPA > PNPB > PNPDPP > PNPTS. Oxime-based functionalized surfactants showed the highest reactivity towards carboxylic esters[20,40] compared to phosphate and sulphonate esters. The nucleophilic reactivity of these $\alpha$-nucleophiles towards S═O centre is less than P═O centre because the S═O centre shows less electrophilicity than the P═O electrophilic centre. In the P═O centre, due to strong p$\pi$–d$\pi$ interaction the electrophilicity of central atom P reduces which hinders the attack of $\alpha$-nucleophile in the rate determining step. In contrast, the non-existence of p$\pi$–d$\pi$ bonding manifested to the highest reactivity of C═O ester. In the case of *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl benzoate (PNPB), PNPA hydrolyzed very fast compared to PNPB in the presence of series (IA) functionalized surfactants. The nucleophilic attack occurs at the electrophilic centre (C═O). The centre is modified by the attached group, R ($CH_3$ or $C_6H_5$). According to Um *et al.*[41] PNPB shows more stable resonance structure compared to PNPA. More stable resonance structure of PNPB is responsible for the decrease in the reactivity of PNPB in nucleophilic substitution reaction in the presence of oxime-based functionalized surfactant.

## EXPERIMENTAL

### Materials

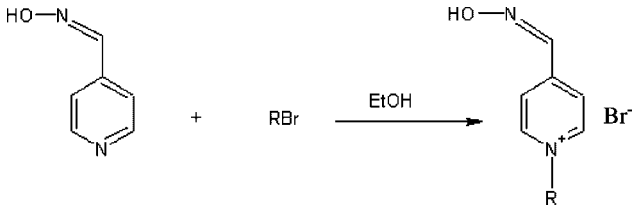
*p*-nitrophenyl acetate (PNPA) was procured from Fluka (USA) and *p*-nitrophenyl benzoate (PNPB) was procured from Lancaster (Lancashire, England). *p*-nitrophenyl *p*-toluene sulphonate (PNPTS) and *p*-nitrophenyldiphenyl phosphate (PNPDPP) were

prepared at the Vertox laboratory of Defence Research Development Establishment, Gwalior (India). 3-hydroxyiminomethyl-1-alkylpyridinium bromide series (IA) and 4-hydroxyiminomethyl-1-alkylpyridinium bromide series (IB) functionalized surfactants were prepared in the laboratory of Dr Kamil Kuca by quaternization of pyridine aldoxime with the corresponding alkyl bromides. All solutions were prepared in triple distilled water.

## Methods

### *Preparation of N-alkylpyridinium aldoxime bromides*

Pure pyridine aldoxime in dry ethanol was mixed with 1-bromo alkane-2 in ratio 1:1.4 (Scheme 4). This mixture was refluxed for 40 h. After that, the solution was evaporated and then the crude oil product was recrystallized from ether or ethyl acetate washed with ether and allowed to dry. The recrystallization was accomplished several times to reach the pure product. The process of reaction was controlled by TLC (Kieselgel Merck; mobile phase (Chloroform: Methanol = 100: 1; detection UV 254, Dragendorff reagent). All the functionalized surfactants have been characterized by NMR spectroscopy and melting points. (Melting points of IA and IB series of surfactants are **IA** $C_8$; 95–97 °C, $C_{10}$; 101–103 °C, $C_{12}$; 141–143 °C, $C_{14}$; 124–125 °C, $C_{16}$; 107–109 °C, **IB** $C_8$; 109–111 °C, $C_{10}$; 119–120 °C, $C_{12}$; 129–130 °C, $C_{14}$; 130–132 °C, $C_{16}$; 140–142 °C).




**Scheme 4.**

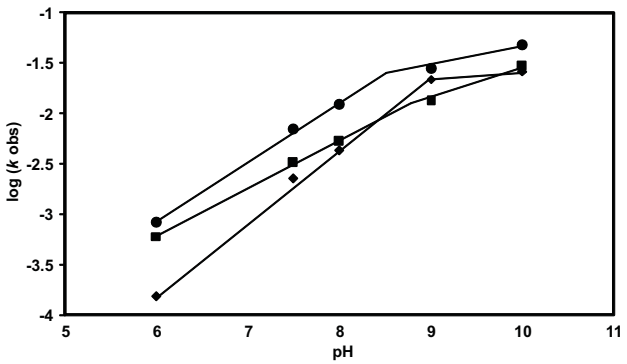



**Figure 3.** pH-rate log constant profiles for the cleavage of *p*-nitrophenyl acetate (PNPA) in the presence of 3-hydroxyiminomethyl-1-alkyl pyridinium bromide ($C_8$, $C_{10}$, $C_{12}$,) at different pH. $C_8$-(◆), $C_{10}$-(■) and $C_{12}$-(●). This figure is available in colour online at www.interscience.wiley.com/journal/poc

### *Determination of p$K_a$*

The p$K_a$ values of IA and IB series of functionalized surfactant were determined by kinetic and spectrophotometric methods.[42]

### *Kinetic method*

The apparent p$K_a$ values of some oxime-based functionalized nucleophiles of IA series have been determined by measuring the first-order rate constant for the hydrolysis of PNPA at different pH values (6–10) in the presence of these nucleophiles. The rate data indicate that the rate of reaction increases with increase in pH values. Plots of log $k_{obs}$ versus pH (Fig. 3) showed breaks at definite pH values. This break point was taken as p$K_a$ apparent for the nucleophiles. The p$K_a$ values obtained by the kinetic method agreed well with those measured by the UV spectrophotometer (Table 2).

### *Spectrophotometric method*

The apparent p$K_a$ of IA and IB series of functionalized surfactants having different alkyl chain lengths ($C_8$, $C_{10}$, $C_{12}$, $C_{14}$, $C_{16}$) were determined spectrophotometrically. An aliquot (3 ml) of a stock solution ($5.0 \times 10^{-4}$ M) of the functionalized surfactant in 50% (v/v) acetonitrile was diluted with 25 ml phosphate buffer solution of pH 7.1. The pH of the solution was measured by using Systronics (Type-362) pH-meter and the spectrum was recorded using buffer solution as a blank. The absorption spectrum of this solution was recorded using Varian Cary 50 UV-visible spectrophotometer in the range of 200–400 nm and at different pH values. The absorbance at (295 nm) for IA series and (339 nm) for IB series was plotted against the pH of the buffer solutions. The sigmoidal curves (Fig. 4) were obtained and p$K_a$ values were

**Table 2.** Acid ionization constants (p$K_a$) of (IA and IB) series of functionalized surfactants having different alkyl chain lengths ($C_8$, $C_{10}$, $C_{12}$, $C_{14}$, $C_{16}$) by spectrophotometric and kinetic method

| | p$K_a$ | | |
|---|---|---|---|
| | IA series | | IB series |
| Functionalized surfactant | Spectrophotometric method | Kinetic method | Spectrophotometric method |
| $C_8$ | 8.9 | 9.0 | 8.2 |
| $C_{10}$ | 9.0 | 8.8 | 8.1 |
| $C_{12}$ | 9.0 | 8.9 | 8.2 |
| $C_{14}$ | 9.1 | — | 8.1 |
| $C_{16}$ | 8.6 | — | 7.8 |

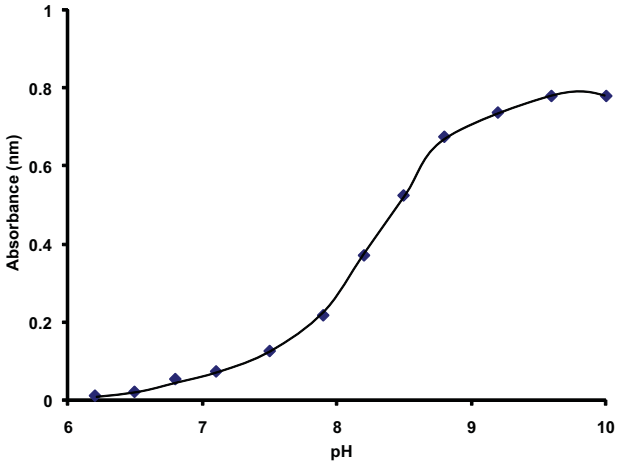



**Figure 4.** Plot between pH and absorbance for 4-hydroxyiminomethyl-1-dodecylpyridinium bromide at 339 nm.

calculated based on three determinations around the point of half neutralization using equation 1

$$pK_a = pH_{exp} - \log \frac{Abs_{\Psi} - Abs_{HOx}}{Abs_{Ox} - Abs_{\Psi}} \quad (1)$$

where $Abs_{\psi}$ is the absorbance of partially ionized (at pH observed) form of oxime, $Abs_{HOx}$ is the absorbance of unionized form of oxime and $Abs_{Ox}$ is the absorbance of fully ionized form of oxime.

p$K_a$ values of these surfactants (4 and 3-hydroxyiminomethyl-1-alkylpyridinium bromide) are recorded in Table 2. Two representative spectra of IA and IB series at different pH values are shown in Figs 5 and 6.

*Determination of critical micelle concentration (CMC)*

The CMC of each functionalized surfactant was determined by electrical conductivity measurements at 27 °C by plotting the specific conductance of surfactant solutions as a function of its concentrations. The observed CMC values are given in Table 3.

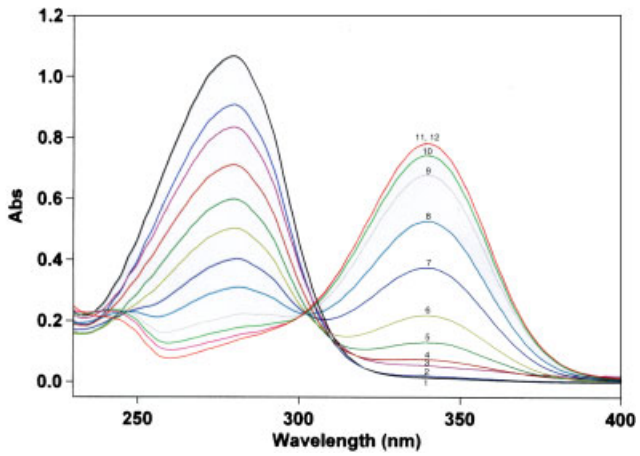



**Figure 5.** Absorption spectra of 4-Hydroxyiminomethyl-1-decylpyridinium bromide at different pH values. $5.3 \times 10^{-5}$ M; in 50% (v/v) acetonitrile-water, 25 °C. Run and pH: (1) 6.2; (2) 6.5; (3) 6.8; (4) 7.1; (5) 7.5; (6) 7.9; (7) 8.2; (8) 8.5; (9) 8.8; (10) 9.2; (11) 9.6; (12) 10.0. This figure is available in colour online at www.interscience.wiley.com/journal/poc

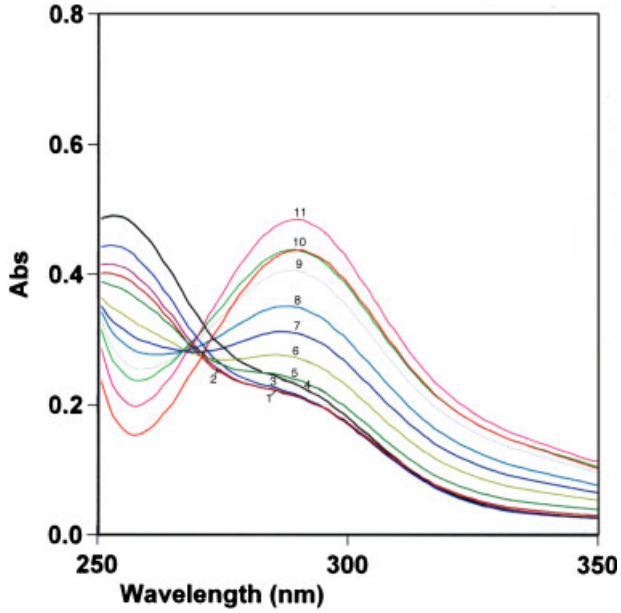



**Figure 6.** Absorption spectra of 3-Hydroxyiminomethyl-1-tetradecyl-pyridinium bromide at different pH values. $5.3 \times 10^{-5}$ M; in 50% (v/v) acetonitrile-water, 25 °C. Run and pH: (1) 7.2; (2) 7.5; (3) 7.8; (4) 8.3; (5) 8.9; (6) 9.4; (7) 9.6; (8) 9.8; (9) 10.0; (10) 10.5. This figure is available in colour online at www.interscience.wiley.com/journal/poc

*Kinetics measurements*

The rate of nucleophilic reaction was determined at 27 °C ± 0.2 °C by monitoring the increase in the absorption of *p*-nitrophenoxide anion (400 nm) using a Varian Cary 50 UV-visible spectrophotometer equipped with a peltier temperature controller unit. The kinetic study was performed under pseudo-first order conditions with the concentration of nucleophile in excess over the substrate concentration and at an ionic strength of 0.1 M (with KCl). The initial concentration of the substrate was $5.0 \times 10^{-5}$ M for all reactions. Phosphate buffer was employed to control the pH of the media. The pH of the reaction medium was measured using Systronics (Type-362) pH-meter. The dependence of the observed first-order rate constant $k_{obs}$ ($s^{-1}$) on the overall aldoxime concentration is typical of processes in which the reactive species is the major buffer component ($Ox^-$). *p*-nitrophenoxide ion was liberated quantitatively and identified as one of the products by comparing the UV-visible spectrum at

**Table 3.** Critical micelle concentration (CMC) of (IA, IB) series of functionalized surfactants having different alkyl chain lengths ($C_8$, $C_{10}$, $C_{12}$, $C_{14}$, $C_{16}$) by conductometric method

| Functionalized surfactant | CMC (mM) | |
|---|---|---|
| | IA series | IB series |
| $C_8$ | 4.2 | 3.0 |
| $C_{10}$ | 2.3 | 1.8 |
| $C_{12}$ | 1.26 | — |
| $C_{14}$ | 0.73 | — |
| $C_{16}$ | 0.053 | — |

the end of the reaction with the authentic sample under the experimental condition.

## CONCLUSIONS

An important objective of this study was to determine the kinetic efficiencies of oxime-based functionalized surfactants series (IA and IB) for the cleavage of carboxylic, phosphate and sulphonate esters, which are assumed as model representative of organophosphate and nerve agents. Series IA and IB functionalized surfactants are effective functionalized surfactants and can be used as a novel micellar catalyst under mild conditions. The results of their study could potentially be useful for the designing of more effective organophosphorus antidotes.

## Acknowledgements

The authors are grateful to Professor Rama Pande, Head, School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur (Chattisgarh), India for providing laboratory facilities. They are also thankful to Pt. Ravishankar Shukla University, Raipur (Chattisgarh), India for providing university fellowship to one of the authors (Shuchi Tiwari) of this paper. This work was also supported by Czech Ministry of Defence project N o. OVUOFVZ200803.

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