Research Article

Journal of Physical Organic Chemistry

Received: 7 March 2013, Revised: 23 April 2013, Accepted: 29 April 2013, Published online in Wiley Online Library: 18 June 2013

(wileyonlinelibrary.com) DOI: 10.1002/poc.3142

Reactivity studies of carbon, phosphorus and sulfur-based acyl sites with tertiary oximes in gemini surfactants

Bhanushree Gupta[a], Rahul Sharma[a], Namrata Singh[a], Yevgen Karpichev[b], Manmohan L. Satnami[a] and Kallol K. Ghosh[a]*

Kinetic studies of the reactions of tertiary oximes (monoisonitroso acetone; MINA and butane 2,3 dione monooxime; BDMO) with some carboxylate (*p*-nitrophenyl acetate and *p*-nitrophenyl benzoate), phosphate (*p*-nitrophenyl diphenyl phosphate and bis (2,4-dinitrophenyl) phosphate) and sulfonate (*p*-nitrophenyl *p*-toluene sulphonate) esters in gemini surfactants have been conducted. The observed first-order rate constant versus surfactant profiles show micelle-assisted bimolecular reactions involving interfacial ion exchange between bulk aqueous media and micellar pseudophase. Experimental results showed that MINA exhibited better nucleophilic activity towards ester cleavage than BDMO. Pseudophase model has been applied in order to determine micellar second-order rate constants and binding constants. Copyright © 2013 John Wiley & Sons, Ltd.

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

Keywords: α-nucleophile; tertiary oxime; gemini surfactant; organophosphates; kinetics

INTRODUCTION

The facile hydrolysis of organophosphate esters is ubiquitous and has drawn great attention due to the importance in various chemical and biological reactions.[1–5] These highly toxic, lipophilic and life-threatening compounds are used as chemical warfare agents (sarin, soman, tabun, etc.), pesticides and insecticides[6] (parathion, paraoxon, diazinon, etc.). Due to extreme toxicity, safety and other licensing reasons, few molecules, known as simulants or surrogates, are used to find mechanism of their hydrolysis.[7] Carboxylate, phosphate and sulphonate esters are few existing simulants exhibiting limited toxicity and are comparatively less expensive as well. They mimic similar behavior as nerve agents and can be employed as a safer substrate with less vigorous laboratory settings.[8] Hence, different types of nucleophiles (oximates,[9] hydroxamates,[10] peroxides,[11,12] *o*-iodosocarboxylates,[13] hydroxybenzotriazoles,[14–16] functionalized surfactants,[17] etc.) along with amphiphilic moieties, metallosurfactants,[18] solid supports and latexes[19,20]have been applied as hydrolytic micellar catalysts.[21–23] For many years, efforts have been devoted to design and evaluate the efficiency of α-nucleophiles as decontaminants by several research groups.[24–29] The most systematic study of the effect of a series of α-nucleophiles oximates with pK_a values in the range of 7.7–11.8 on the degradation of pesticide fenitrothion in cationic miceller media, has been provided by Buncel *et al.*,[30] and further kinetic data were interpreted in terms of pseudophase ion exchange model. Nucleophilic substitution of *p*-nitrophenyl diphenyl phosphate (PNPDPP) with butanedione mono-oximate in aqueous cetyltrimethylammonium bromide were performed by Ruasse and workers.[31] The reaction of hydroxylamine with 2,4-dinitrophenyl diethyl phosphate have been monitored by Nome research group.[32] The group[33,34] further examined the hydrolysis of diester bis (2,4-dinitrophenyl) phosphate (BDNPP) with benzohydroximate anion kinetically. Recently, Renard[35] *et al*. synthesized a series of new α-nucleophiles (oximes and amidoximes) and examined their ability to cleave P–S bond of organophosphorus nerve agents. Oximes are potent α-effect nucleophiles, as they exhibit characteristic reactivity than that predicted by Bronsted-type relationship of nucleophilicity and basicity.[36] Tertiary oximes are uncharged oximes and are proved to be better reactivating agents for inhibited cholinesterase in the central nervous system (CNS).[37,38] Monoisonitroso acetone (MINA) (pK_a = 8.34) is highly lipid soluble oxime, which can easily penetrate the blood–brain barrier to reactivate inhibited AChE in CNS.[39]

It is an established fact that micelles and other self-organized assemblies enhance the reactivity of nucleophiles.[40] Currently, some novel surfactants have been reported,[41,42] which produce different types of micellar aggregates upon solubilization in water. Among all the surfactants, gemini[43,44] seems to be an attractive host due to lower critical micelle concentration (CMC), high surface activity, low Krafft point, higher viscoelasticity and enhanced tendency to lower the oil–water interfacial tension in comparison to other conventional surfactants.[45–47] Several research groups[48,49] have been investigating the micellar-

---

* *Correspondence to: K. K. Ghosh, School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur (C.G), 492010, India.*
E-mail: kallolkghosh@yahoo.com

a *B. Gupta, R. Sharma, N. Singh, M. L. Satnami, K. K. Ghosh*
School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, C.G, 492010, India

b *Y. Karpichev*
L.M. Litvinenko Institute of Physical Organic and Coal Chemistry, Donetsk 83114, Ukraine

catalyzed hydrolysis of various toxic and non-toxic simulants using α-effect nucleophiles. Generally, the standard simulants are persistent and hydrophobic in nature; therefore, aqueous solutions of micellar aggregates are employed for their hydrolysis and dephosphorylation reactions. Bhattacharya[50] *et al*. have examined the esterolytic reaction of phosphotriesters (*p*-nitrophenyl diphenyl phosphate and *p*-nitrophenyl hexanoate) in cationic micellar media using 4,4′-(dialkylamino)pyridine-based nucleophiles. Many research groups[51,52] have investigated the hydrolysis of different esters using butane 2,3 dione monooxime (BDMO) as a cleaving agent. A comparative study of catalytic hydrolysis of carboxylate esters using conventional and cationic gemini surfactant has been monitored by Zeng[53] and co-workers. Gemini surfactants containing hydroxyl and ester groups in spacer have recently been synthesized, and alkaline hydrolysis of paraoxon (4-nitrophenyl diethyl phosphate) and arminum (4-nitrophenyl diethyl phosphonate) in the presence of gemini micelles was studied by Popov[54,55] and research group.

To the best of our knowledge very limited work has been done in the detoxification of chemical simulants using tertiary oximes in water-soluble gemini micellar media. Over the last few years, we have examined the catalytic efficiencies of various α-nucleophiles against ester hydrolysis in self-organized systems.[56–61] As a continuation of these investigations herein, we have examined the nucleophilic micellar-mediated hydrolytic reactions of (shown in Chart 1 and Scheme 1) *p*-nitrophenyl acetate (PNPA), *p*-nitrophenyl benzoate (PNPB), PNPDPP, BDNPP and *p*-nitrophenyl *p*-toluene sulphonate (PNPTS) using MINA at pH 9.0 at 27 °C. The observed rate constants were compared with that of BDMO. Two cationic water-soluble gemini surfactants (alkanediyl-α,ω bis (hydroxyethylmethylhexadecylammonium bromide), 16-s-16, MEA $2Br^-$ (s = 4, 6) have been used as micellar catalysts. The acid dissociation constants (pK_a) of both the nucleophiles have also been determined kinetically and spectrophotometrically.

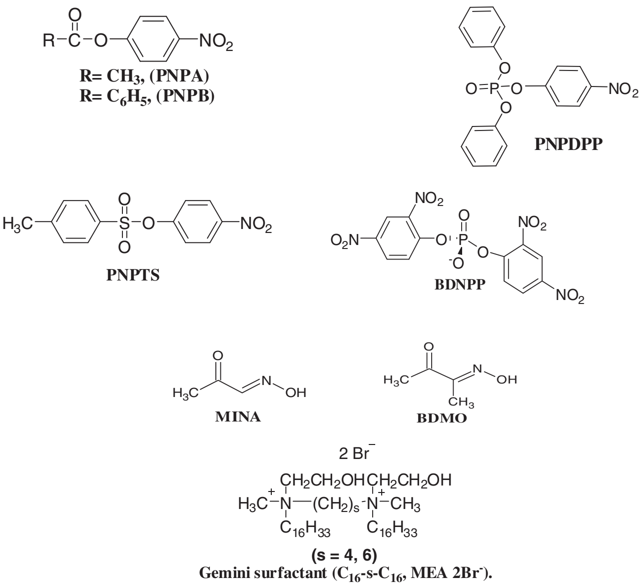


Chart 1. Substrates, nucleophiles and surfactants used in the present investigation

MATERIALS AND METHOD

Materials

PNPA was procured from Fluka (USA), and PNPB was procured from Lancaster (Lancashire, England). PNPDPP and PNPTS were prepared at Defence Research Development Establishment, Gwalior (India), and bis(2,4-dinitrophenyl) phosphate (BDNPP) was synthesized in the Department of Chemistry, Federal University of Santa Catarina, Florianopolis-SC, Brazil. Dimeric gemini surfactants were synthesized in the laboratory of P. Quagliotto, Department of Chemistry, University of Torino, Torino, Italy. MINA and BDMO were purchased from Sigma/Aldrich (St. Louis, Missouri, U.S.A). All solutions of oximes were prepared in triple distilled water.

Methods

Surface tension measurement

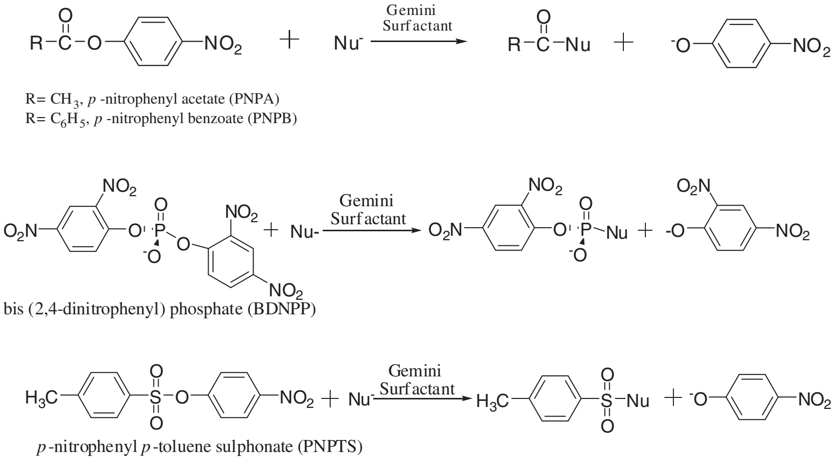
The surface tension of investigated gemini surfactants at pH 9.0 was determined with a surface tensiometer (Jencon, India) using a platinum ring by the ring detachment technique. The tensiometer was calibrated against distilled water. Platinum ring was thoroughly cleaned and dried before each measurement. The ring was hung to the balance, dipped into the solution and then pulled out. The maximum force needed to pull the ring through the interface was measured and correlated to the surface tension. Each experiment was repeated several times until good reproducibility was achieved. The results were accurate within ±0.1 mNm^{-1}.

Determination of acid dissociation constant (pK_a)

The acid dissociation constant (pK_a) values of both the tertiary oximes were determined in absence and presence of 0.25 mM of 16-s-16 MEA $2Br^-$ spectrophotometrically by using the method of Albert and Sergeant.[62] The method depends on the direct determination of the ratio of molecular species (protonated) to dissociated (deprotonated) species in buffer solutions. An aliquot (3 ml) of a stock solution (5×10^{-4} M) of oxime in triple distilled water was diluted with 25 ml phosphate buffer solution. Different pH values ranging from 7.12 to 10.5 were selected to determine the pK_a values of oximes. The pH of the solution was measured using Systronics (Type-362) pH-meter, and the spectrum was recorded using buffer solution as a blank. The absorption spectrum was recorded using Varian Cary 50 UV–VIS spectrophotometer in the range of 200–400 nm in the solutions of different acidity. The average values of ten measurements were considered as the pK_a of the compound with respect to oximino functionality. The spectrophotometric determination of pK_a of MINA is reproduced in Fig. 4 at a temperature 27 °C. The pK_a calculations were made around half neutralization using following equation:

$$\mathrm{p}K_a = \mathrm{pH}_{exp} - \log\frac{\mathrm{Abs}_{\Psi} - \mathrm{Abs}_{\mathrm{HOx}}}{\mathrm{Abs}_{\mathrm{ox}} - \mathrm{Abs}_{\Psi}} \qquad (1)$$

Where, $\mathrm{Abs}_{\mathrm{HOx}}$ is the absorbance of unionized form of compound, Abs_{ψ} is the absorbance of partially ionized form of compound and $\mathrm{Abs}_{\mathrm{Ox}}$ is the absorbance of completely ionized form of compound.



Scheme 1. Nucleophilic attack of Nu⁻ (tertiary oximate ions) at C = O, P = O and S = O centers

Kinetic measurements

The reactions were studied spectrophotometrically with a Varian Cary 50 spectrophotometer by monitoring the appearance of the leaving *p*-nitrophenoxide (for PNPA, PNPB, PNPDPP and PNPTS) and 2,4-dinitrophenoxide ion (for BDNPP) ion at 400 nm at 27 ± 0.2 °C as represented in Fig. 1. Entire kinetic experiments were performed at an ionic strength of 0.1 M KCl. Each experiment was repeated at least twice, and the observed rate constants were found to be reproducible within a precision of about 3% or better. Phosphate buffer (0.1 M) was employed to control the pH of the media. All the pH measurements were obtained using a Systronics pH meter (type 362). The reactions were conducted under pseudo-first-order conditions, i.e. large excess of oximate anions over the substrate (1:10). For all the kinetic runs, the absorbance/time result fits very well with the first-order rate Eqn 2.

$$\ln(A_\infty - A_t) = \ln(A_\infty - A_\mathbf{0}) - kt \qquad (2)$$

The pseudo-first-order rate constants (k_{obs}) were determined from the plots of absorbance versus time with A_0, A_t and A_∞ being the absorbance values at zero, time and infinite time, respectively. The substrate (PNPA, PNPB, PNPDPP, BDNPP and PNPTS) concentration was kept same for all the reactions (0.5×10^{-4} M). The kinetic study was performed at various concentrations of gemini surfactant to investigate the effect of surfactant on the cleaving efficiency of oximes.

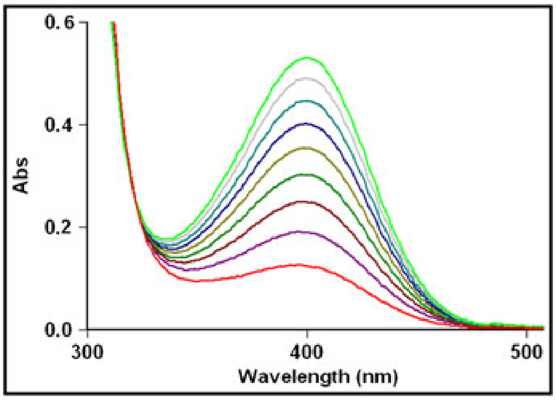


Figure 1. UV spectra collected at different reaction times showing the increase in absorbance of *p*-nitrophenoxide ion for the cleavage of PNPB with BDMO in the presence of gemini surfactant (C_{16}-6-C_{16}, MEA $2Br^-$). Reaction conditions: [PNPB] = 0.5×10^{-4} M, [BDMO] = 0.5×10^{-3} M, [KCl] = 0.1 M, [16-s-16] = 0.5×10^{-3} M, pH = 9.0, Temp. = 27 °C

RESULTS AND DISCUSSION

We have studied the surface properties of investigated gemini surfactants in water and buffer medium inclusive of their proficiency as strong micellar catalyst for various esterolytic reactions. The comparative nucleophilic efficacy of both the tertiary oximes has also been examined by the means of pH effect, nucleophilic effect, substrate effect and by applying the cationic gemini micro-organized media as a catalyst. The pseudo-first-order rate constants were determined for all the kinetic runs.

Surface properties of gemini surfactants in buffer medium

With the surface tension measurements, several parameters referring to interfacial properties have been determined at pH 9.0: (i) Surface excess concentration of surfactant (Γ_{max}) and (ii) minimum area per molecule at the air–water interface (A_{min}) were determined from surface tension data using Eqns (3) and (4)

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left[\frac{d\gamma}{d\log C}\right]_{T,\ P} \qquad (3)$$

$$A_{min} = 1/N\,\Gamma_{max} \qquad (4)$$

Where, R is the gas constant (8.314 $J mol^{-1} K^{-1}$), T is the absolute temperature, C is the surfactant concentration, ($d\gamma/d\log C$) is the slope of the γ versus logC plot taken at the CMC and N is Avogadro's number. Here, constant (prefactor) $n = 3$ for investigated cationic gemini surfactant system which is made up of a divalent surfactant ion and two univalent counterions.[63,64] The value of the surface pressure at the CMC (π_{CMC}) was obtained from Eqn (5),

$$\pi_{cmc} = \gamma_o - \gamma_{CMC} \qquad (5)$$

where γ_o indicates the surface tension of pure solvent, and γ_{CMC} is the surface tension at the CMC. This parameter shows that the maximum reduction of surface tension is due to the adsorption of surfactant molecules and observed when surfactant begins to micellize and not adsorb anymore at the surfaces.[65] Therefore, it demonstrates the effectiveness of the surface tension reduction. Hence, greater the π_{CMC} values, higher the effectiveness of the surfactants π_{CMC} values are listed in Table 1.

Gemini surfactants has extremely low CMC (as presented in Fig. 2), and this unusual tendency of low CMC is due to conformational changes and higher magnitude of energy of transfer coming from both the tails.[66,67] The low CMC for 16-s-16 MEA $2Br^-$ are in general agreement with the reported values previously at 30 °C.[61] It is confirmed from the Table 1 that CMC of MEA-type surfactants reduce significantly in the buffer medium as compared to the aqueous solution of 16-s-16 type cationic gemini surfactants indicating that pH has a direct effect on surface properties. This is clearly inferred from the observed data that, there is very little increase in the values of π_{CMC} and A_{min} as spacer chain length increases from 4 to 6 where as Γ_{max} decreases. The calculated surface properties indicate that spacer chain length effect is not much pronounced in the investigated gemini surfactants.

Acid dissociation constant (pK_a)

As oximate anion takes part in the hydrolysis reaction, it was necessary to follow the pK_a and pH effect on the deprotonation of the oximes. The pK_a of both the oximes were determined spectrophotometrically and kinetically (Fig. 3). The observed values are in good agreement with the literature values.[39,52] To follow the effect of surfactants under the reaction medium on the acid dissociation constants, pK_a of nucleophiles have been determined in the absence and presence of 0.25 mM gemini surfactants. It can be concluded from the Table 2 that, pK_a of both the nucleophiles decrease slightly in the presence of gemini surfactants illustrating increased ionization of nucleophiles in miceller core. Hence, the observed results favor the shift of acid base equilibria (Scheme 2) and accounts for the higher rate constants. Observed p*K*a values support MINA to be superior Nu^- than BDMO.

Effect of pH

Study of pH effect helps to evaluate the p*K*a of Nu^- and enables to control the reaction rate at preferable conditions. In support of the above mentioned facts, the effect of pH was studied on cleavage of carboxylate ester with 0.5×10^{-3} M of MINA. It was observed that the rate of reaction increased with the rise in pH. A pH versus rate constant profile for the nucleophilic cleavage of PNPA and PNPB by MINA ion gave the apparent p*K*a value (8.40) for the MINA as represented in Fig. 4 (a). Typically, the pseudo-first-order rate constants for reaction of PNPA were determined at different pH values between 6.7 and 11.0. The significant effect of pH was observed on pseudo-first order rate constant rate of the nucleophilic reactions. The most prominent advantage observed from these experiments were at pH > p*K*a, due to the appearance of completely dissociated oxime functionality ($-CH=NO^-$).

Figure 4 (a) represents the plots of k_{obs} and fraction of MINA ionized (degree of nucleophilic dissociation; α) versus pH for the reaction of PNPA with MINA. Owing to the assumptions, the ionization state of MINA (Nu^-) is responsible for the catalysis in nucleophilic aided hydrolysis reaction. Hence, Eqn (6) may give the actual value of k_{obs}.

$$k_{obs}^{HA} = k_{obs}^{0} + k_{HA} - [HA]_T \, \alpha_{HA^-} \tag{6}$$

Nucleophile MINA has only one proton active site which releases the reactive species as shown in Eqn (7)

$$k_{obs} = k_{obs}^{0} + k_{MINA} - [MINA]_T \, \alpha_{MINHA-} \tag{7}$$

Since α^-_{MINA} is equal to $K_a/K_a + [H^+]$ and K_a represents kinetically apparent dissociation constant of MINA, it is confirmed that at pH 9.0, i.e. above the pK_a of MINA, mono-anion is the reactive species.[56–59]

Effect of nucleophile [Nu^-]

The nucleophilic concentration-dependent first-order rate constants were determined spectrophotometrically for the reaction

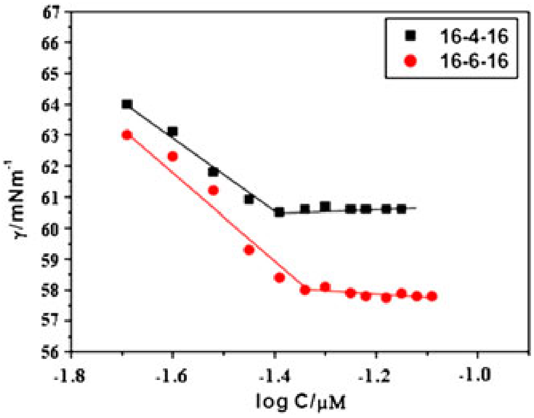
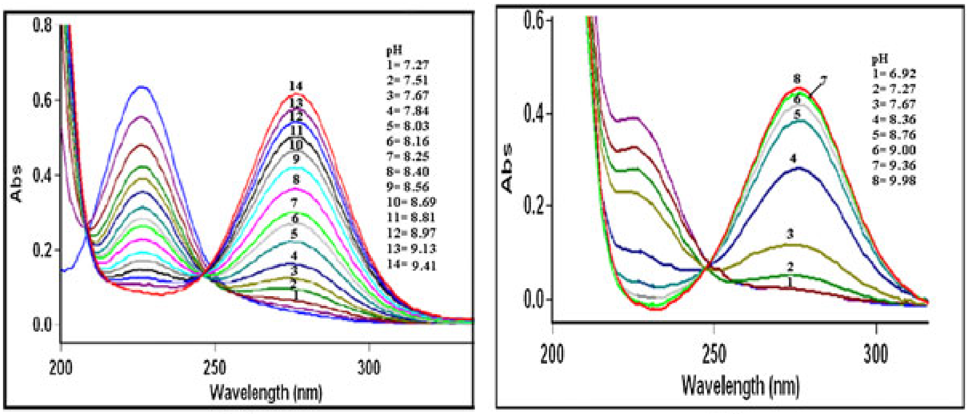


Figure 2. Plots of surface tension versus log conc. of C_{16}-s-C_{16}, MEA $2Br^-$ at pH 9.0

Table 1. Surface properties of gemini surfactants (C_{16}-s-C_{16}, MEA $2Br^-$) in water and buffer medium (pH = 9.0)

Surfactants	Medium	CMC(μM)	Π_{CMC} mNm^{-1}	Γ_{max} 10^6 $mol\,m^{-2}$	A_{min} 10^{20} m^2
C_{16}-4-C_{16}, MEA $2Br^-$	Water[a]	2.000	32.0	1.390	119.4
	Buffer	0.035	7.50	0.417	398.1
C_{16}-6-C_{16}, MEA $2Br^-$	Water[a]	3.000	34.0	1.270	130.7
	Buffer	0.045	10.9	0.405	409.9

[a] Ref 41,42



(a) (b)

Figure 3. Representative absorption spectra of MINA, c = 5.3 × 10^{-5} M; in water, Temp.=27 °C. (a) in the absence of gemini surfactants at different pH values. (b) in the presence of gemini surfactants at different pH values

Table 2. Acid dissociation constants (pK_a) of MINA and BDMO [0.2 ×10^{-4} M] in the absence and presence of 16-s −16 MEA 2Br^- (2 5 × 10^{-4} M) by spectrophotometric method at Temp. = 27 °C

Gemini surfactant	pK_a	
	MINA	BDMO
Nil	8.40	9.50
16-4-16	8.11	9.02
16-6-16	8.15	9.10

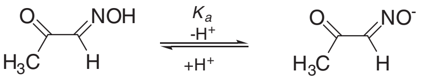
of PNPA, PNPB and BDNPP with MINA in excess, at 27 °C and pH 9.0, as shown in Fig. 5. The data for reaction of carboxylate and phosphate esters with different concentrations of MINA and BDMO at pH 9.0 is summarized in Table 3.

The obtained kinetic data completely supports the hypothesis that tertiary oximate anion act as nucleophilic catalyst for the hydrolysis of both the esters. Here, Eqn (8) describes the reaction of carboxylate and phosphate esters with MINA, and k_0 corresponds to the intercept of the k_{obs} versus [Nu^-] plot in Fig. 5.

$$\boldsymbol{k_{obs} = k_0 + k_{Nu}{}^{-}[Nu^{-}]} \qquad (8)$$

$$\boldsymbol{k_0 = k_{H2O} + k_{OH}{}^{-}[OH^{-}]} \qquad (9)$$

The term k_{H2O} in Eqn (9) represents the rate constant for very weak nucleophile at very low OH^- concentration.[56–59] At higher pH, the intercept is governed by the term $k\,{}^{-}_{OH}$. Figure 5 gave a straight line with intercept k_0 indicating no competition with other nucleophiles as OH^-, H_2O for PNPB and BDNPP. However, in the case of hydrolysis of PNPA, there is a contributory effect of OH^- and H_2O (followed Eqn 8). However, the whole hydrolysis reaction for PNPA, PNPB and BDNPP at large concentration of nucleophiles can be represented as



Scheme 2. pH-dependent ionization of monoisonitroso acetone

$$\boldsymbol{k_{obs} = k_{Nu}{}^{-}[Nu^{-}]} \qquad (10)$$

Table 4 provides apparent second-order rate constants for both the nucleophiles against different substrates. Observed values of $k_{2,app}$ support MINA to have higher rate constants over BDMO for all the esters. Taking into account deprotonation degrees of both nucleophiles at pH 9.0, we can calculate their nucleophilicities (see Table 4). Indeed, MINA falls on the Bronsted plot for low basicity nucleophiles (pK_a ≤ 9.0) characterized by the slope α_{Nu} ca. 0.5[9,18] whereas BDMO falls on the leveling-off Bronsted plot for the oximate ions with pK_a ≥ 9.0 having negligible sensitivity to the oxime strucuture. (α_{Nu} ≈0). Thus, the two tertiary oximes, MINA and BDMO, have a difference in acidity constants of one order of magnitude with only two to three times difference in the nucleophilicities.

Effect of gemini surfactants on the hydrolysis of different esters

The kinetic plots shown in Fig. 6 represent variation of the absorption of 4-nitrophenoxide ion of (PNPA) and (PNPB) with time at pH 9.0 for the reaction of MINA with esters in the presence of 0.5 mM 16-4-16 MEA 2Br^-. The plots correspond to formation of 4-nitrophenoxide ions in the system as a result of substrate dissociation. Pseudo-first-order rate constants (k_{obs}) for the nucleophilic cleavage of five different esters (PNPA, PNPB, PNPDPP, BDNPP and PNPTS) in the presence of cationic gemini surfactants have been summarized in Table 5 and illustrated in Fig. 7. Among all the investigated esters, cationic gemini surfactants displayed the highest catalytic activity towards the hydrolysis of carboxylate ester; PNPA and lowest activity for the sulphonate ester PNPTS.

The hydrolytic property of MINA and BDMO was executed from the rate constant versus [gemini surfactant] profiles

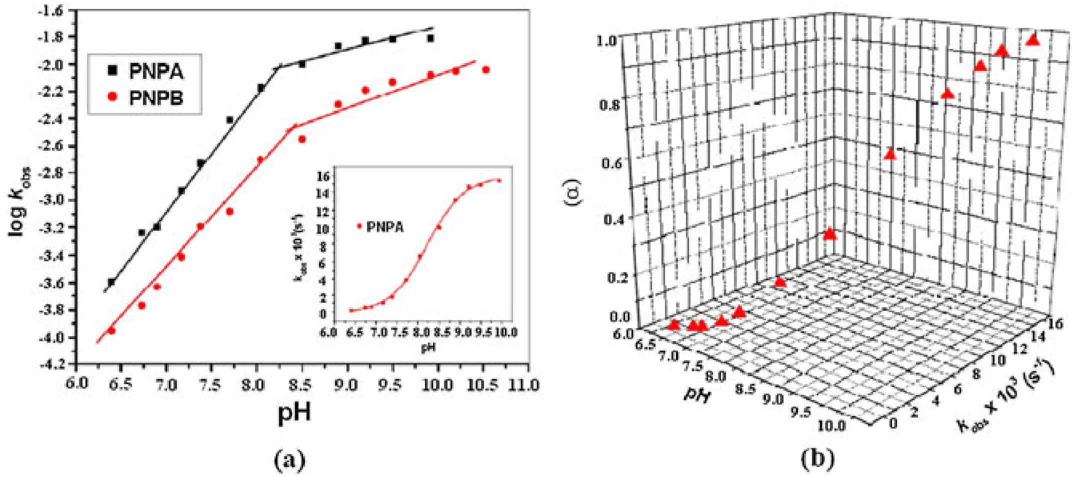


Figure 4. (a) Plots of log k_{obs} versus pH for PNPA and PNPB with MINA (Inset): Plot of first-order rate constants versus pH for the reaction of PNPA with MINA. (b) Plot of k_{obs} and α versus pH for the reaction of PNPA with MINA. Reaction conditions: [Substrate] = 0.5 × 10^{-4} M, [MINA] = 0.5 × 10^{-3} M, [KCl] = 0.1 M, Temp. = 27 °C

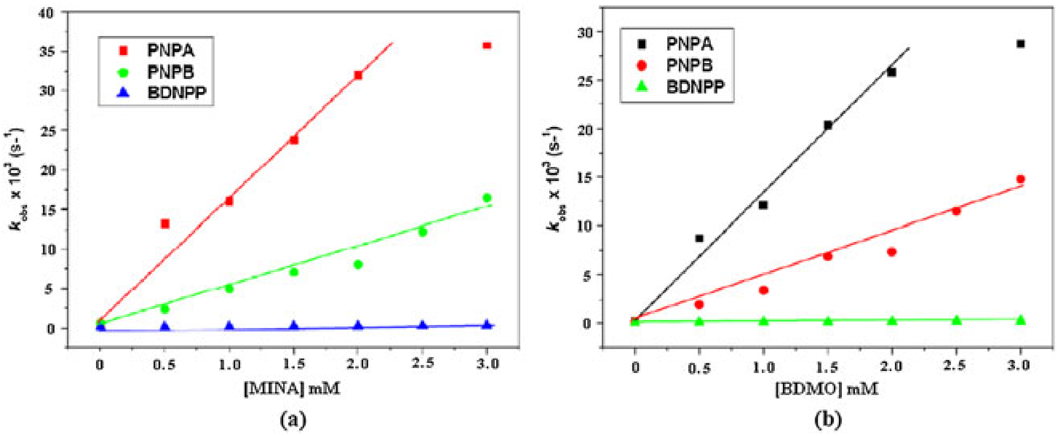


Figure 5. Plots for the nucleophilic effect of MINA on the hydrolysis of PNPA and PNPB (a) MINA (b) BDMO

(Fig. 7 and Fig. S1.) for cleavage of different esters at C = O, P = O and S = O centers. The observed rate constants were dependent on both the type of nucleophile and gemini surfactant used. The hydrolysis of carboxylate esters by MINA was facile (PNPA: 3.56 fold PNPB: 2.90 fold) as compared to BDMO (PNPA: 2.95 PNPB: 1.98 fold) in cationic gemini micellar media. Similarly, the cleavage of PNPDPP (2.10 fold), BDNPP (1.68 fold) and PNPTS (1.06 fold) was easier in MINA as compared to BDMO (PNPDPP: 1.79 fold, BDNPP: 1.13 fold PNPTS: 1.02 fold).

Rate-surfactant profile shows that the rate of reaction increases with increasing surfactant concentration up to a certain concentration and then decreases at higher concentration of surfactants. The trend supports a typical micellar-assisted bimolecular reactions. The rate maxima are independent of the type of surfactants, but the magnitude of rate constant depends on type of surfactants. The observed rate maxima are due to the dilution effect of enhanced concentration of gemini surfactant.[65] Gemini surfactants, linked by different spacer groups, offer di-cationic head group that is significantly higher in electrostatic interactions. Hydrophobicity of substrate and properties of surfactant undoubtedly play key role for the hydrolytic reactions in micellar media.[66–68] Preferably, increasing concentration of surfactant releases more cationic gemini micelles and initially results in increased rate of reaction. Due to the conformational changes, cationic gemini surfactants bring reactants in close proximity by binding the substrates via hydrophobically binding and coulombically attracting the negatively charged nucleophile[11,12] As the number of micelles increases, all the substrate molecules get associated in the micellar phase. Hence, further increment of surfactant enhances the number of micelles which take up the oximate anions into the volume element of micellar-assisted reaction by deactivating the substrate. As a consequence of this, substrate bound to one micelle becomes unable to react with nucleophile in another.[52,56–59] It is evident from the observed data (Table 5) that 16-4-16 MEA 2Br$^-$ gemini surfactants are slightly more efficient catalyst for the hydrolytic reactions as compared to 16-6-16 MEA 2Br$^-$ surfactants. It may be due to the low CMC which favors the immediate micelles formation and provides higher aggregation number in the reaction media at the same total surfactant concentration.[60] Another important factor which supports 16-4-16 to be a better catalyst is the spacer chain length (s = 4) in comparison to 16-6-16 (s = 6). If s = 4, elongated spherical or cylindrical micelles are likely forming

Table 3. Nucleophilic effect on the hydrolysis of carboxylate esters using 1 = MINA and 2 = BDMO

$[Nu^-]$ mM	$k_{obs} \times 10^3$ (s^{-1})					
	PNPA		PNPB		BDNPP	
	1	2	1	2	1	2
Nil	0.476	0.189	0.578	0.131	0.058	0.031
0.5	13.2	8.74	2.32	1.91	0.141	0.079
1	16.0	12.1	4.88	3.37	0.179	0.109
1.5	26.8	20.4	7.01	6.87	0.205	0.137
2.0	32.0	25.8	8.03	7.34	0.251	0.169
2.5	-	26.4	12.2	11.5	0.298	0.205
3.0	35.7	28.7	16.5	14.8	0.345	0.241

Reaction conditions: [Substrate] = 0.5×10^{-4} M, [KCl] = 0.1 M, pH = 9.0, Temp. = 27 °C

Table 4. Second-order rate constants for $[Nu^-]$ against different substrates

Substrate	Second-order rate constant k_2 ($M^{-1} s^{-1}$)	
	MINA	BDMO
PNPA	14.6	40.5
PNPB	6.3	20.0
PNPDPP	1.83	4.0
BDNPP	0.111	0.28
PNPTS	0.005[a]	0.015[a]

[a]Estimated from Bronsted plot Ref 16: 25 °C

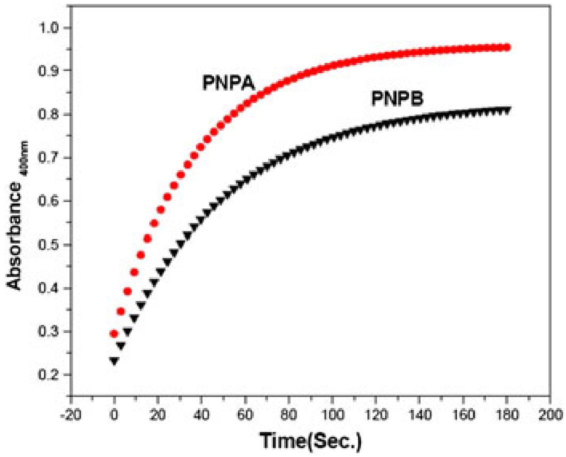


Figure 6. Time-dependent increase of absorbance at 400 nm upon hydrolysis of PNPA and PNPB (at pH 9.0) by oximate ion in the presence of gemini 16-4-16 MEA $2Br^-$. Reaction conditions: [MINA] and [16-4-16] = 0.5 × 10–3 M. Substrate concentrations: [PNPA] and [PNPB] = 0.5×10^{-4} M, Temp. = 27 °C

with increased viscoelasticity, but in s = 6 prolate micelles are formed with decreased aggregation properties. Hence, 16-4-16 MEA $2Br^-$ proved to be proficient[11,12] with better kinetic results of micellar catalysis. It is noteworthy that the two gemini surfactants provide high observed reaction rates along with low Krafft temperature caused by introducing OH^- groups into head groups. The latter structure modifications allow us to use gemini surfactant at considerably high concentrations without a co-surfactant at room temperature. Another factor is the change of the microenvironment due to the presence of OH^- groups which makes micellar interface less water deficient and therefore facilitates reactions involving charged species.[54,55]

Application of pseudophase model (PPM)

The effect of micelles on the bimolecular reactions is quantitatively rationalized by the PPM (Berezin approach).[69–72] This approach treats micelles and a solvent (water) both as distinct reaction phases. The overall reaction rates depend on the concentration of reactants including rate constants. The whole reaction rates are depicted by the sum of the rate in each distinct phase.

In the case of our reaction systems, there are two reactive species: hydroxide ions from bulk aqueous phase and oximate ions produced by tertiary oximes. We assume that the presence of gemini surfactants very slightly change the pK_a of tertiary oximes in water (see Table 2); hence, scheme 3 can be proposed. In this scheme, (S), OH^- and Ox^- represent substrate, hydroxide ions and oximate ions, respectively. Superscript w and m indicate aqueous phase and micellar pseudophase in the reaction. Substrate is mainly cleaved by oximates. As it can be seen from Bronsted plots for oximate ions,[9,18] reactivities of MINA and OH^- ions are comparable, but observed reaction rates in water for oximes under chosen conditions are more than 10 times higher. The role of hydroxide ions at pH 9.0 is minor; hence, we can apply PPM[73–75] taking into account the main route (oxymolysis) and alkaline hydrolysis enhanced by micelles of gemini surfactants:

$$k_{obsd} = \frac{\left(k^{m}_{2,Ox}/V_M\right)\cdot K_S\cdot K_{Ox}\cdot C + k^{w}_{2}}{(1+K_S\cdot C)\cdot(1+K_{Ox}\cdot C)}\cdot\frac{K_{a,app}}{K_{a,app}+a_{H^+}}[Ox]_0 + \frac{\left(k^{m}_{2,OH}/V_M\right)\cdot K_S\cdot K_{OH}\cdot C + k^{w}_{OH}}{(1+K_S\cdot C)\cdot(1+K_{OH}\cdot C)}[OH]_0 \qquad (11)$$

Table 5. Effect of gemini surfactants on the hydrolysis of various esters: GS: gemini surfactants (1) 16-4-16 MEA 2Br$^-$, (2) 16-6-16 MEA 2Br$^-$

[G S] (mM)	$k_{obs} \times 10^3$ (s^{-1})																			
	PNPA				PNPB				PNPDPP				BDNPP				PNPTS			
	MINA		BDMO		MINA		BDMO		MINA		BDMO		MINA		BDMO		MINA		BDMO	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Nil	13.2	13.2	8.74	8.74	2.32	2.32	1.91	1.91	0.86	0.86	0.803	0.803	0.141	0.141	0.079	0.079	0.087	0.087	0.066	0.066
0.25	38.4	24.9	31.2	12.4	32.6	17.8	18.3	7.21	19.1	12.3	11.2	7.5	0.333	0.273	0.297	0.256	0.276	0.218	0.268	0.136
0.50	47.8	30.9	40.5	17.8	42.5	21.9	30.2	11.9	23.1	18.38	12.56	10.43	0.378	0.318	0.370	0.315	0.289	0.258	0.294	0.191
1.0	60.1	40.1	54.3	23.3	51.3	33.0	41.9	18.6	25.6	16.73	13.84	10.28	0.399	0.325	0.383	0.328	0.303	0.285	0.323	0.257
1.50	75.3	37.3	63.4	30.8	59.5	28.5	42.3	23.9	24.1	15.12	13.1	10.1	0.421	0.348	0.394	0.318	0.318	0.273	0.345	0.253
2.0	79.8	33.4	61.9	28.3	64.6	21.0	36.6	19.2	22.6	14.03	11.11	9.38	0.439	0.351	0.374	0.326	0.320	0.273	0.339	0.279
2.50	83.2	34.2	60.4	26.6	62.9	21.5	38.8	18.4	23.0	14.1	11.56	9.49	0.412	0.349	0.350	0.303	0.317	0.281	0.330	0.275
3.0	78.9	32.9	60.2	27.4	60.3	20.3	37.8	20.8	21.0	12.9	10.28	9.41	0.416	0.347	0.362	0.301	0.314	0.293	0.329	0.274
4.0	79.1	33.0	60.8	38.0	61.0	21.2	38.0	19.7	22.0	13.1	10.9	9.52	0.418	0.346	0.365	0.304	0.315	0.295	0.327	0.276
5.0	78.8	33.1	61.0	37.9	61.5	21.4	38.1	20.5	23.7	12.5	11.0	9.50	0.415	0.348	0.363	0.305	0.316	0.296	0.327	0.279
6.0	79.0	33.4	60.9	37.6	61.3	21.0	37.7	21.0	24.0	13.0	10.7	9.49	0.416	0.346	0.363	0.306	0.314	0.294	0.328	0.277

[Substrate] = 0.5 × 10^{-4} M, [Nu$^-$] = 0.5 × 10^{-3} M, μ = 0.1 M KCl, pH = 9.0, Temp. = 27 °C

Where, k_2^m and k_2^w (M^{-1} s^{-1}) are the second-order rate constants indicating nucleophilicity of the oximate species, K_S (M^{-1}) is the substrate binding equilibrium constant, K_{Ox} is the oxime binding constant, V_M (L/mol) is the partial mole volume of surfactant, C (M) is concentration of micellized surfactant, k_{OH}^w and α_{OH}^- correspond to contribution of alkaline hydrolysis, $K_{a,\,app}$ is apparent constant for acid ionization of oxime in the presence of surfactant, a_H^+ is the proton activity and α is the oximate ion deprotanation degree. We depicted the quantitatively rationalized kinetic data for the cleavage of carboxylate (PNPA), phosphate (PNPDPP) and sulphonate (PNPTS) esters by MINA and BDMO in the presence of 16-4-16 MEA 2Br$^-$ and 16-6-16 MEA 2Br$^-$ in Table 6 and Fig. 8. The kinetic profiles for three substrates are adequately described in terms of PPM. PNPTS and PNPDPP are very hydrophobic ($K_S \geq 3000$ M^{-1}); their concentration profiles reach maximum (optimal concentration, C_{opt}) at D_{tot} lower 1 mM which corresponds ca. 75% binding substrate. PNPA is considerably less hydrophobic (low value of binding constant K_S ca. 250 M^{-1}) and reactive substrate with sufficient alkaline hydrolysis route which can be satisfactorily predicted using Eqn (11); see Fig. 8 c,d.

At 3 mM, about 40% of PNPA is incorporated in the micellar pseudophase. This allows nucleophiles, both OH$^-$ ion and oximate ions, to cleave esters in micelle with the observed rates of almost one order of magnitude higher than in water. The OH$^-$ ion binding is low and can be assumed to be 30 to 50 M^{-1}[54,55] that makes oxymolysis the main route in the micellar pseudophase. As it can seen from the Table 6, binding constant of oximate ions is lower for 16-6-16 MEA almost for all the systems, irrespective of substrate, that makes 16-4-16 MEA more efficient surfactant in the studied reactions.

The nucleophilicities of oximate ions (parameter k_m/V_M in Table 6) are somewhat smaller than in water, and correct estimation of the intrinsic nucleophilicities requires the knowledge of V_M. For conventional surfactants, it was considered to be from 0.14 (estimated Stern volume) to 0.34[66,67] sometimes, a value of 0.5 was used.[64] For gemini surfactants, this value might be different since the gemini micelles have smaller aggregation numbers and can elongate to form rod-like micelles at relatively low concentrations. As it can be seen from Table 6, the effect of substrate concentration caused by binding both substrate and nucleophile in the micellar pseudophase is the main factor determining rate enhancement in the presence of gemini micelles under mild pH conditions.

Comparative efficacy of tertiary oximes

In order to compare the reactivity of both the tertiary oximes MINA and BDMO, the rate of hydrolysis of PNPA, PNPB, PNPDPP, BDNPP and PNPTS has been evaluated. According to data presented in Table 3, MINA shows better nucleophilic efficiency than butane 2,3-dione monoxime towards different electrophilic centers (C = O, P = O and S = O centers). The reactivity difference of both the nucleophiles can be explained on the basis of their acid dissociation constant (pK_a). Lower pK_a of MINA (pK_a = 8.30)[39] as compared to BDMO (pK_a = 9.50)[37] increases the electron withdrawing effect of MINA; hence, it provides sufficient concentration of oximate anions to the cleavage of various substrate.

Changing the electrophilic centers from carbonyl to phosphonyl or to sulphonyl group can visualize significant effect on their electrophilicity. The order of reactivity for all the substrates can be

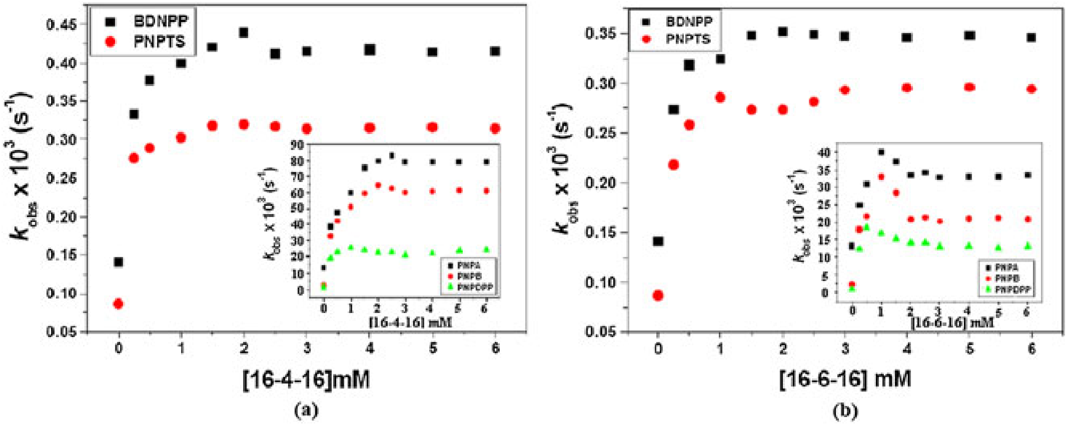
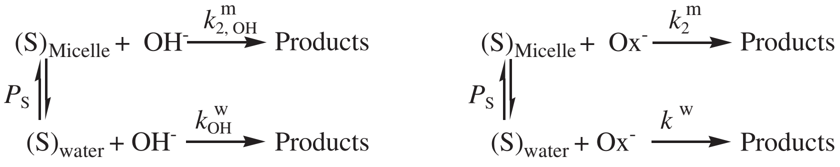


Figure 7. Observed rate constant for the hydrolysis of BDNPP and PNPTS by MINA as a function of [16-s-16], (s = 4, 6), pH 9.0 at Temp.=27 °C in borate buffer 0.01 M. (Inset). Observed rate constant for the hydrolysis of PNPA, PNPB and PNPDPP as function of [16-s-16], (s = 4, 6) pH = 9.0 at Temp.=27 °C in borate buffer 0.01 M



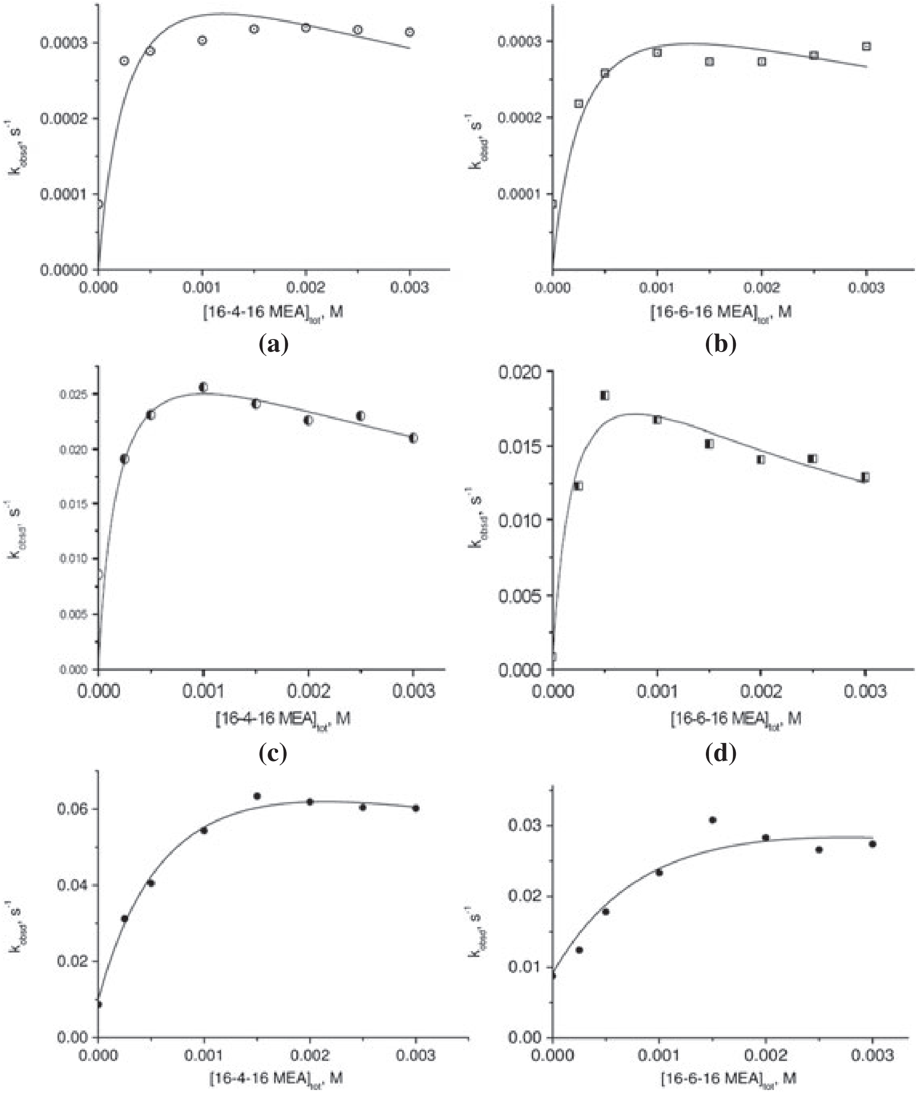
Scheme 3. Schematic distribution of reactive spices in aqueous and micellar phase

Table 6. Kinetic parameters obtained by applying pseudophase model

Nu^-	Gemini surfactant	k_2^w ($M^{-1} \cdot s^{-1}$)	α (at pH 9.0)	k_m/V_M (s^{-1})	K_S (M^{-1})	K_{ox^-}(M^{-1})
PNPTS						
MINA	16-4-16	0.005	0.89	0.006	3000	230
	16-6-16	0.005	0.88	0.011	3000	190
BDMO	16-4-16	0.015	0.49	0.012	3000	200
	16-6-16	0.015	0.44	0.02	2000	100
PNPA						
MINA	16-4-16	14.6	0.89	2.0	250	580
	16-6-16	14.6	0.88	1.2	250	350
BDMO	16-4-16	40.5	0.49	2.4	250	750
	16-6-16	40.5	0.44	1.5	250	410
PNPDPP						
MINA	16-4-16	1.64	0.89	0.4	5000	200
	16-6-16	1.64	0.88	0.2	4000	350
BDMO	16-4-16	4.0	0.49	0.3	5000	280
	16-6-16	4.0	0.44	0.4	5000	160

Reaction conditions: [Substrate] = 0.5 × 10^{-4} M, [MINA] = 0.5 × 10^{-3} M, KCl = 0.1 M, pH = 9.0, Temp. = 27 °C

depicted as PNPA > PNPB > PNPDPP > BDNPP > PNPTS. The nucleophilic efficacy of both the nucleophiles is quite less towards the suphonyl ester when compared to phosphonyl and carboxyl esters.[50,65] This difference may be due to least electrophilicity of S = O center, than P = O and C = O centers. The comparative reactivity of phosphate and carboxylate esters can be accounted on the basis of reduced electrophilicity of P = O center due to pπ–dπ interaction, which hinders the attack of nucleophile in rate determining step. On the contrary, the absence of pπ–dπ bonding at C = O center results in facile hydrolysis of carboxylate esters. Among the carboxylate esters (PNPA and PNPB), PNPA was hydrolyzed extremely fast in the presence of only oximes and micelle-assisted oximes. This can be accounted on the basis of high stability of PNPB as compared to PNPA[52] that leads to decreased reactivity in all the nucleophilic substitution reactions.



(a) (b)

(c) (d)

(e) (f)

Figure 8. Plots for the effect of gemini surfactants for the cleavage of PNPTS by MINA, (a) 16-4-16, (b) 16-6- 16; PNPDPP by MINA, (c) 16-4-16 (d) 16-6-16; PNPA by BDMO, (e) 16-4-16, (f) 16-6-16; Reaction conditions: [Substrate] = 0.5×10^{-4} M, [MINA] = [BDMO] = 0.5×10^{-3} M, KCl = 0.1 M, pH = 9.0, Temp. = 27 °C (lines predicted with model)

CONCLUSIONS

The present investigation was performed to determine the kinetic efficiencies of tertiary oxime-based reactivators against various simulants of chemical warfare agents. With this motive, different esters were selected as substrate. The nucleophile MINA showed better nucleophilicity than BDMO for all the hydrolysis reactions at pH 9.0, which makes it model candidate for decontamination reactions. Gemini surfactant-assisted hydrolysis showed tremendous enhancement in the rate of reactions, and the effects were analyzed in terms of PPM. The observed first-order rate constants were found to increase with increasing surfactant concentration, which further remains almost constant at a higher surfactant concentration, showing the nature of micellar-catalyzed reactions and can be accounted on the basis of surface properties and of pK_a of nucleophiles in the presence of surfactant. Results of this investigation are useful in developing an effective mechanism for the degradation of chemical and biological warfare agents under potential therapy for the treatment of human exposure.

Acknowledgement

BG and NS are grateful to Pt. Ravishankar Shukla University, Raipur for providing university fellowship.

REFERENCES

[1] A. C. Hengge, I. Onyido, *Curr. Org. Chem.* **2005**, *9*, 61.
[2] Y. C. Yang, J. A. Baker, J. R. Ward, *Chem. Rev.* **1992**, *92*, 1729.
[3] W. W. Cleland, A. C. Hengge, *Chem. Rev.* **2006**, *106*, 3252.
[4] B. M. Smith, *Chem. Soc. Rev.* **2008**, *37*, 470.
[5] A. C. Hengge, *Adv. Phys. Org. Chem.* **2005**, *40*, 49.
[6] C. A. Bunton, A. Blasko, N. D. Gillitt, *Langmuir* **1997**, *13*, 6439.

[7] K. Kim, O. G. Tsay, D. A. Atwood, D. G. Churchill, *Chem. Rev.* **2011**, *111*, 5345.
[8] D. Mandal, B. Mondal, A. K. Das, *J. Phys. Chem. A* **2010**, *114*, 10717.
[9] E. Buncel, C. Cannes, A. P. Chatrousse, F. Terrier, *J. Am. Chem. Soc.* **2002**, *124*, 8766.
[10] R. S. Mello, E. S. Orth, W. Loh, H. D. Fiedler, F. Nome, *Langmuir* **2011**, *27*, 15112.
[11] S. Bhattacharya, K. Snehalatha, *J. Org. Chem.* **1997**, *62*, 2198.
[12] S. Bhattacharya, K. Snehalatha, P. V. Kumar, *J. Org. Chem.* **2003**, *68*, 2741.
[13] H. Morales-Rojas, R. A. Moss, *Chem. Rev.* **2002**, *102*, 2497.
[14] S. Clandia, P. Rossi, F. Felluga, F. Formaggio, M. Palumbo, P. Tecilla, C. Toniolo, P. Scrimin, *J. Am. Chem. Soc.* **2001**, *123*, 3169.
[15] Y. S. Simanenko, T. M. Prokop'eva, A. F. Popov, C. A. Bunton, E. A. Karpichev, V. A. Savelova, K. K. Ghosh, *Russ. J. Org. Chem.* **2004**, *40*, 1337.
[16] T. M. Prokop'eva, Y. S. Simanenko, I. P. Suprun, V. A. Savelova, T. M. Zubareva, E. A. Karpichev, *Russ. J. Org. Chem.* **2001**, *37*, 655.
[17] N. Singh, Y. Karpichev, B. Gupta, M. L. Satnami, J. Marek, K. Kuca, K. K. Ghosh, *J. Phys. Chem. B* **2013**,*117*, 3806.
[18] S. K. Bhattacharya, N. Kumar, *Coord. Chem. Rev.* **2009**, *253*, 2133.
[19] R. B. Karabacak, M. Erdem, H. Turk, *Colloids Surf. A Phys.Eg ASP* **2011**, *377*, 167.
[20] M. Erdom, H. Turk, *React. Func. Polym.* **2008**, *68*, 321.
[21] J. Yan, R. Breslow, *Tetrahedron Lett.* **2000**, *41*, 2059.
[22] F. Mancin, P. Tecilla, U. Tonellato, *Langmuir* **2000**, *16*, 227.
[23] Y. C. Yang, L. L. Szafraniec, W. T. Beandry, C. A. Bunton, *J. Org. Chem.* **1993**, *58*, 6964.
[24] I. H. Um, Y. H. Shin, S. E. Lee, K. Yang, E. Buncel, *J. Org. Chem.* **2008**, *73*, 923.
[25] R. M. Tarkka, E. Buncel, *J. Am. Chem. Soc.* **1995**, *117*, 1503.
[26] R. Nagelkerke, G. R. J. Thatcher, E. Buncel, *Org. Biomol. Chem.* **2003**, *1*, 163.
[27] F. Terrier, P. R. Dafonte, E. L. Guevel, G. Moutiers, *Org. Biomol. Chem.* **2006**, *4*, 4352.
[28] A. F. Popov, *Pure Appl. Chem.* **2008**, *80*, 1381.
[29] E. Buncel, I. H. Um, *Tetrahedron* **2004**, *60*, 7801.
[30] X. Han, V. K. Balakrishanan, G. W. van Loon, E. Buncel, *Langmuir* **2006**, *22*, 9009.
[31] N. Ouarti, A. Marques, I. Blagoeva, M. F. Ruasse, *Langmuir* **2000**, *16*, 2157.
[32] A. J. Kirby, B. S. Souza, M. Medeiros, J. P. Priebe, A. M. Manfredi, F. Nome, *Chem. Comm.* **2008**, 4428.
[33] E. S. Orth, P. L. F. Da Silva, R. S. Mello, C. A. Bunton, H. M. S. Milagre, M. N. Eberlin, H. D. Fiedler, F. Nome, *J. Org. Chem.* **2009**, *74*, 5011.
[34] A. J. Kirby, J. R. Mora, F. Nome, *Biochim. Biophys. Acta* **2013**, *1834*, 454.
[35] G. S. Andre, M. Kliachyna, S. Kodepelly, L. L. Leriche, E. Gillon, P. Y. Renard, F. Nachon, R. Baati, A. Wagner, *Tetrahedron* **2011**, *67*, 6352.
[36] K. K. Ghosh, J. Vaidya, M. L. Satnami, *Int. J. Chem. Kinet.* **2006**, *38*, 26.
[37] Z. Radic, R. K. Sit, Z. Kovarik, S. Berend, E. Garcia, L. Zhang, G. Amitai, C. Green, B. Radić, V. V. Fokin, K. B. Sharpless, P. Taylor, *J. Biolog. Chem.* **2012**, *287*, 11798.
[38] T. M. Shih, J. W. Skovira, J. C. O'Donnell, J. H. McDonough, *J. Mol. Neurosci.* **2010**, *40*, 63.
[39] J. Kalisiak, E. C. Ralph, J. Zhang, J. R. Cashman, *J. Med. Chem.* **2011**, *54*, 3319.
[40] S. De, V. K. Aswal, P. S. Goyal, S. Bhattacharya, *J. Phys. Chem.* **1996**, *100*, 11664.
[41] J. Toullec, M. Moukawim, *Chem. Commun.* **1996**, 221.
[42] Kabir-ud-Din, P. A. Koya, Z. A. Khan, *J. Colloid Interface Sci.* **2010**, *342*, 340.
[43] D. Tikariha, K. K. Ghosh, P. Quagliotto, S. Ghosh, *J. Chem. Eng. Data* **2010**, *55*, 4162.
[44] D. Tikariha, N. Singh, M. L. Satnami, K. K. Ghosh, N. Barbero, P. Quagliotto, *Colloids Surf., A* **2012**, *411*, 1.
[45] L. G. Qui, X. Jiang, L. N. Gu, G. Hu, *J. Mol. Catal. A: Chemical* **2007**, *277*, 15.
[46] S. Kolay, K. K. Ghosh, P. Quagliotto, *Colloids Surf. A* **2009**, *348*, 234.
[47] K. Holmberg, *Adv. Colloid Interface Sci.* **1994**, *51*, 137.
[48] S. Bhattacharya, V. P. Kumar, *Langmuir* **2005**, *21*, 71.
[49] K. K. Ghosh, S. Kolay, S. Bal, M. L. Satnami, P. Quagliotto, P. R. Dafonte, *Colloid Polym. Sci.* **2008**, *286*, 293.
[50] S. Bhattacharya, V. P. Kumar, *J. Org. Chem.* **2004**, *69*, 559.
[51] (a) B. Kumar, M. L. Satnami, K. K. Ghosh, K. Kuca, *J. Phys. Org. Chem.* **2012**, *25*, 864. (b) B. Kumar, D. Tikariha, K. K. Ghosh, N. Barbero, P. Quagliotto, *J. Phys. Org. Chem.* **2013**. DOI. 10.1002/poc.3141
[52] S. Tiwari, S. Kolay, K. K. Ghosh, K. Kuca, J. Marek, *Int. J. Chem. Kinet.* **2009**, *41*, 57.
[53] J. Bing-Ying, Z. Rong-Rong, X. Jia-Qing, D. Juan, M. Xiang-Guang, Z. Xian-Cheng, *J. Disp. Sci. Tech.* **2005**, *26*, 105.
[54] T. M. Zubareva, A. V. Anikeev, E. A. Karpichev, I. V. Kapitanov, T. M. Prokop'eva, A. F. Popov, *Theor. Exp. Chem.* **2011**, *47*, 108.
[55] T. M. Zubareva, A. V. Anikeev, E. A. Karpichev, A. N. Red'ko, T. M. Prokop'eva, A. F. Popov, *Theor. Exp. Chem.* **2012**, *47*, 377.
[56] M. L. Satnami, S. Dhritlahre, R. Nagwanshi, I. Karbhal, K. K. Ghosh, F. Nome, *J. Phys. Chem. B* **2010**, *114*, 16759.
[57] S. Bal, M. L. Satnami, S. Kolay, R. M. Palepu, P. R. Dafonte, K. K. Ghosh, *J. Surf. Sci. Technol.* **2007**, *23*, 33.
[58] N. Singh, K. K. Ghosh, J. Marek, K. Kuca, *Int. J. Chem. Kinet.* **2011**, *43*, 569.
[59] N. Singh, K. K. Ghosh, J. Marek, K. Kuca, *Ind. J. Chem. B* **2012**, *51*, 611.
[60] D. Tikariha, B. Kumar, N. Singh, K. K. Ghosh, P. Quagliotto, *J. Surfact. Deterg.* **2011**, *14*, 555.
[61] V. Sharma, M. Borse, V. K. Aswal, N. K. Pokhriyal, J. V. Joshi, P. S. Goyal, S. Devi, *J. Colloid Interface Sci.* **2004**, *277*, 450.
[62] A. Albert, E. P. Sergeant. *Determinations of Ionization Constants, A Laboratory Manual*. Chapman and Hall Press, London, **1971**.
[63] B. Kumar, D. Tikariha, K. K. Ghosh, *J. Dispersion Sci. Technol.* **2012**, *33*, 265.
[64] B. Kumar, D. Tikariha, K. K. Ghosh, P. Quagliotto, *J. Mol. Liq.* **2012**, *172*, 81.
[65] K. K. Ghosh, M. L. Satnami, *Colloids Surf. A Physicochem. Eng. Asp.* **2006**, *274*, 125.
[66] M. A. Mir, J. M. Khan, R. H. Khan, A. A. Dar, G. M. Rather, *J. Phys. Chem. B* **2012**, *116*, 5711.
[67] M. Tian, Y. Fan, G. Ji, Y. Wang, *Langmuir* **2012**, *28*, 12005.
[68] W. Jiang, B. Xu, J. Zhong, J. Li, F. Liu, *J. Chem. Sci.* **2008**, *4*, 411.
[69] K. K. Ghosh, D. Sinha, M. L. Satnami, D. K. Dubey, P. R. Dafonte, G. L. Mundhara, *Langmuir* **2005**, *21*, 8664.
[70] C. A. Bunton, G. Savelli, *Adv. Phys. Org. Chem.* **1986**, *22*, 213.
[71] C. A. Bunton, *J. Mol. Liq.* **1997**, *72*, 231.
[72] I. V. Kapitanov, I. A. Belousova, M. K. Turovskaya, E. A. Karpichev, T. M. Prokop'eva, A. F. Popov, *Russ. J. Org. Chem.* **2012**, *5*, 651.
[73] C. A. Bunton, *Adv. Coll. Int. Sci.* **2006**, *333*, 123.
[74] C. A. Bunton, F. Nome, F. H. Quina, L. S. Romsted, *Acc. Chem. Res.* **1991**, *24*(12), 357.
[75] I. H. Um, J. Y. Lee, S. Y. Bac, E. Buncel, *Can. J. Chem.* **2005**, *83*, 1365.