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Oxime functionality in surfactant self-assembly: An overview on combating toxicity of organophosphates

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ABSTRACT

There is an immediate need to develop new strategies for detoxification and decontamination of organophosphorus-containing nerve agents and pesticides. Oximes have witnessed increased scientific interest because of their various applications ranging from acetylcholinesterase reactivators, independent alpha nucleophiles to functionalized nano-aggregates against organophosphate toxicity. The role of oximes as supernucleophilic systems in detoxification reactions is an important research theme and substantial efforts have been made in this report to address this fact. The results have been rationalized in terms of micellar kinetic studies in relation to the oxime structure. The reactivity of oximate ions in cationic micelles, as functionalized aggregates, as reactive polymers and metallomicelles has been well reviewed. Amidoximes emerging as versatile tool in detoxification chemistry has been discussed marginally in the present report. This article motivates similar kinds of studies from different viewpoints. Such studies can be extended to other micellar systems with versatile hydrophobic and hydrophilic properties.

Contents

1. Introduction and scope

Organophosphates include a large variety of compounds with different physical, chemical and biological properties including toxicity [1]. Intentional, accidental and occupational OP poisoning is a major

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health problem and the use of organophosphorus nerve agents by terrorist groups in recent years is posing a great threat [1–2]. The broadest spectrum of these compounds is used as pesticides and chemical warfare agents. Exposure to even small amount of these organophosphorus compounds (OPCs) is fatal and may result into death due to respiratory failure. In developing countries, the number of cases of exposures and poisonings is much greater because of lack of protective measures and regulatory restrictions. The 1995 sarin gas attack in the Tokyo subway and the August 2013 attack on civilians in Syria have driven the urgency to cease the misuse of chemical warfare agents demanding a serious measure towards degradation of such toxic chemicals [3]. The main toxic mechanism of OPCs is the irreversible inhibition of the cholinesterases (ChE) such as acetylcholinesterase (AChE) or butyrylcholinesterase (BChE) and other related esterases at the muscarinic and nicotinic synapses. Human exposure to OPCs results in acute poisoning (so called cholinergic crisis) — manifested by salivation, tremors, respiratory paralysis, hypotension, and with more extreme exposure to death [4–6]. The general structure of OPCs that act as ChE inhibitors is shown in Fig. 1.

OPCs exhibit marked variation of action depending on the substituents R_1, R_2 and X. The extreme toxicity is associated with those compounds in which X is a strong electronegative group such as halide, cyanide or thiocyanate. Due to the day-to-day applications of these OPCs as pesticides their facile hydrolysis is of theoretical and practical interest. Chemical decontamination of these toxic esters requires systems that may ensure:

- Commercial availability and high reactivity of the reagents and cost effectivity
- Broad spectrum applicability of the system against all kinds of chemical warfare agents
- Environmentally benign reactions between the system and toxic substrates
- Chemical stability of the system
- Efficacy of the decontamination system under mild conditions.

Destruction of carboxylate, phosphate and sulfonate based esters is of prime significance and several remedies including reactions of various toxic esters with oximes, hydroxamic acids, oximates in micellar solutions, surface active oximes, and peroxides have been suggested. Since the rate of nucleophile-aided hydrolysis of esters is enhanced by cationic micelles, a variety of surfactant-based reagents incorporating peroxides, iodosylcarboxylates and oxime functionality have been developed [7–8]. Oximate ions (–CH═NO$^-$) are important tools in kinetic, mechanistic and biochemical studies. The nucleophilic reactivities of oximate ions are generally believed to be one of the key factors, alone with the affinity for acetylcholinesterase (AChE), affecting the efficacy of ChE reactivators [9–11].

The study of oximes as AChE reactivators is vital in case organophosphate poisoning. Oximes are a particularly appealing class of α-nucleophiles with pK_a values falling in the range of 7 to12 which makes them ideal candidates for decontamination reactions. As α-nucleophile, these have been widely used for cleavage of several toxic OPCs and their simulants [12–13]. The key objective of the present article is to study the micellar catalyzed reactions of OPCs simulants using α-nucleophilic systems especially functionalized aggregates. Hence, information based on toxic nerve agents and their simulants along with their detoxification chemistry are of paramount importance to have intimate understanding of mechanisms involved.

2. Organophosphates and nerve agent poisoning

OPCs comprise of a diverse group of chemicals and majority of them have been shown to result in high levels of acute neurotoxicity and carcinogenicity. OPCs may be broadly categorized into four groups (Fig. 2). Typical representatives of group I are sarin (GB), soman (GD), and cyclosarin (GF); group II is represented by V series compounds (for instance, VX and VR); for group III, tabun (GA) is typical while group IV is represented by GV compound, see Fig. 3.

3. Chemical warfare agents (CWAs) and organophosphorus pesticides

The first organophosphorus (OP) nerve agents, tabun (GA) and shortly thereafter sarin (GB) were developed in the 1930s by Gerhard Schrader in Germany. These, and the more toxic soman (GD) developed in 1944 and cyclosarin (GF) are members of the so-called G series compounds [14–16]. These compounds have emerged as the major nerve agents known to have been produced and weaponized. The frequent terrorist attacks reveal the ease with which these weapons can be utilized [17–18]. The nerve agents are alkylphosphonic acid esters. Tabun contains a cyanide group, and sarin and soman are methylphosphonofluoridate esters containing a fluorine substituent as a leaving group. These nerve agents contain a C—P bond that is almost unique and is not found in other pesticides. This C—P bond is very resistant to hydrolysis. V series agents such as VX and VR contain sulfur atom and are the alkylphosphonothiolates. Considerable efforts are being made to devise methods and materials that may neutralize the hazardous effects of these agents [19–22]. The OP pesticides are one of the most abundant environmental and food chain pollutants, which drew global attention with respect to human, animal and insect health.

For protective measures it is important to know the sources of pollutants and the magnitude of the threat. Hence, the detection method for OPCs in the environment is a prime concern [23]. Structures of some highly toxic CWAs and pesticides that have been widely used for decades in agriculture, medicine and industries due to their high efficiency as pesticides or for typical enzyme inhibition [24–25] are shown in Fig. 3. The hydrolysis of phosphate esters is an important chemical reaction since, these are hydrophobic phosphorus substrates, and their decontamination involves dephosphorylation or hydrolysis [25].

4. Detoxification systems

The toxicity and long-term environmental hazards of OPCs require detailed studies on detoxification mechanisms and development of efficient, readily available and inexpensive systems for their decontamination. A simple and straightforward method for the detoxification of OPCs involves their reactions with α-nucleophiles. Different α-nucleophiles like hydroxamic acid [26–27], *o*-iodosyl carboxylates [28–29], hydroxyl benzotriazoles [30–31], hydroxylamine [32–33], hydrazine [34], and hypochlorite [35] have been used to detoxify OPCs and nerve agents.

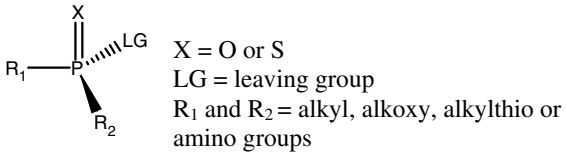


Fig. 1. General structure of organophosphorus compounds.

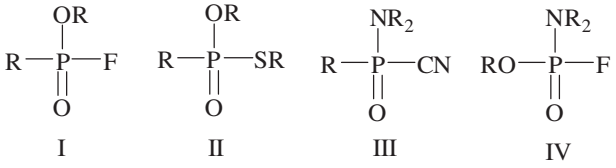


Fig. 2. Groups of organophosphorous compounds.

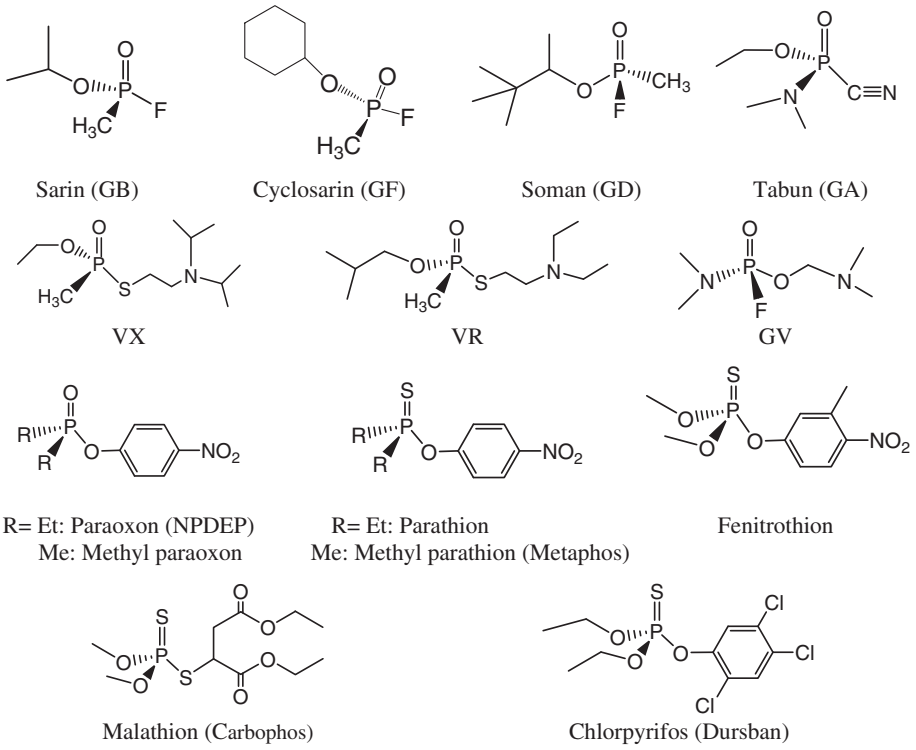


Fig. 3. Nerve agents and organophosphorus pesticides.

Oximes reduce the effects of such hazardous compounds and have attracted attention of scientists worldwide [36–37]. Of these, pyridinium aldoximes have emerged to be effective antidotes against OP-pesticides and nerve agent intoxications. There are extensive evidences to support the ability of pyridinium oximes to reactivate phosphorylated AChE [38–40]. Most of the oximes investigated so far, can be classified into uncharged tertiary and charged quaternary oximes. The latter case oximes having clinical applications can be divided into two groups: quaternary monopyridinium and bispyridinium oximes. Tertiary oximes viz. monoisonitrosoacetone (MINA) and butane-2,3-dione monoxime (BDMO) are strong α-nucleophiles capable of hydrolyzing phosphate ester bonds [24,41]. Oximes such as pralidoxime, HI-6, and obidoxime have been used in the clinical practice to treat intoxication by certain OPCs for decades [42,43]. The current standard treatment of OP poisoning with reactivators includes different types of quaternary oximes with a similar basic structure differing by the number of pyridinium rings and by the position of the oxime group in the pyridinium ring [44]. The more electron withdrawing effect of quaternary nitrogens in pyridinium oxime 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 pyridinium aldoximes and ketoximes ($pK_a \approx 7–10$) provides sufficient concentration of the nucleophilic oximate anion even in neutral solutions. It has also been proved that oximes are actively involved as potent α-nucleophiles in various hydrolytic reactions (Fig. 4) of phosphate diesters and triesters [45, 46].

The fast formation of phosphorylated oxime follows by slow degradation either via hydrolysis with regeneration of the initial oxime (path A) or towards formation of the corresponding nitrile (path B). Since the question of turnover of the nucleophile by hydrolysis of acylated intermediate has been considered in detail several decades ago [8], there was less evidence in dephosphorylation process [47, 48]. According to Epstein et al. [48] the regeneration of the oxime shown in Fig. 4 is a much slower process so it cannot be considered as a true catalyst. The formation of a nitrile as the main product has also been reported for its 2-hydroximinomethyl analog [49]. At the same time, a kinetic evidence of the true catalytic properties has been reported by Bunton et al. [50] for aliphatic trimethylammonium surfactant functionalized with an oxime moiety. Most of the kinetic studies were done by using oximate ion in large excess to follow initial nucleophilic attack. The use of α-nucleophiles as the basis for functionalized nucleophilic systems makes it possible to provide abnormally high rates of nucleophilic cleavage of OPs.

5. Micellar rate effect in organic reactions

Nerve agents and pesticides are organic compounds of low polarity and their chemical decontamination is less effective in aqueous medium due to solubility problem with water soluble reactants, and organic solvent imposes some operational problems in the field conditions. Effects of organized assemblies e.g. micelles [51–53], microemulsions [54] and vesicles on chemical reactivity and the positions of chemical equilibrium have been rationalized in terms of differences between the properties of interfacial and bulk water. In such medium, organic reactants are portioned into the surfactant aggregates by electrostatic and hydrophobic interactions, and the observed rate accelerations are largely due to the increased localization of the reactants. Being used as a reaction medium, micellar solutions may provide considerable benefits in comparison with

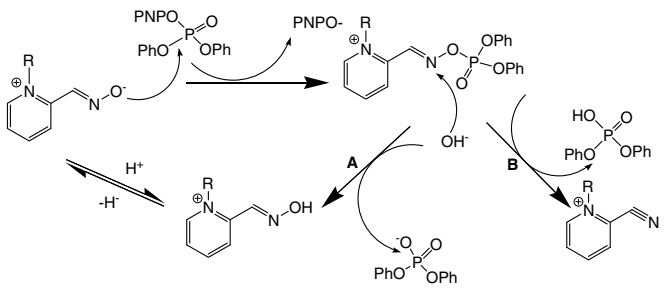


Fig. 4. Mechanism of hydrolysis of organophosphate (NPDPP) as in the case of a pyridinium-2-aldoxime.

homogeneous solutions. Surfactant aggregates and in particular micelles can be regarded as nanosized molecular containers which can capture and concentrate in their small volume lipophilic and ionic species [55].

Quantitative treatments of reactivity in association colloids frequently use the pseudophase model in which micelles and water are assumed to be distinct reaction media, with consideration of reactant concentrations and rate constants in the two regions. One of its primary assumptions is that such an aggregate constitutes a pseudophase, separated from the bulk solution where it is dispersed, so that reagents partition between the bulk phase and the aggregate pseudophase. Thus, bimolecular nucleophilic reactions can be described as illustrated in Fig. 5, where S and Nu are the substrate and the nucleophile in water (subscript w) or in the micellar pseudophase (subscript m), k_2^w and k_2^m are the second-order rate constants for substrate/nucleophile reactions in the aqueous phase and in the micellar pseudophase, respectively, and K_S is the binding constant of the substrate to the micelles based on the concentration of micellized surfactant, defined as the difference in the total concentration of surfactant and the critical micelle concentration (cmc), i.e., $[D] = [\text{surfactant}]_{\text{total}} - \text{cmc}$.

According to the pseudophase partitioning model (PPM), the approach proposed in the early 1970s by the Russian team of Berezin [56], the second-order rate constant k_{2m} is written in terms of the local concentration of the nucleophile in units of moles per liter of reaction volume within the micellar pseudophase (Nu_m), which cannot be measured directly. The concentration of the nucleophile can also be taken as a mole fraction of the bound reactive anion to the micellized surfactant, defined as $Nu_m = [Nu_m]/[D]V_m = \beta/V_m$, where β is the degree of counterion binding to the micelle and V_m is the molar volume of the reactive region in the aggregate. V_m also relates the apparent measurable micellar rate constant, k_m to k_2^m (i.e., $k_m = k_2^m/V_m$). Thus, the observed rates (k_ψ, s^{-1}) of bimolecular reactions under pseudo-first-order conditions ([Nu] ≫ [S]) gives Eq. (1).

$$k_\psi = \frac{k'_w[\text{Nu}] + k_m K_s[\text{D}]}{1 + K_s[\text{D}]} = \frac{k'_w + (k_2^m/V_m)\beta K_s[\text{D}]}{1 + K_s[\text{D}]}. \quad (1)$$

The value of V_m is unknown, so that in order to estimate k_2^m from k_m, one assumes a value for V_m; typical estimates range from 0.14 M^{-1} (the volume of the micellar Stern layer) to 0.37–0.5 M^{-1} (estimated volume of the micelles) [57].

These values allow us to rewrite Eq. (1) using the values of binding constants reflecting the partitioning of both nucleophile and substrate in the following form:

$$k_\psi = \frac{k'_w + \left(k_{2,m}/V_m\right)K_{Nu}K_s[\text{D}]}{(1 + K_s[\text{D}])\quad(1 + K_{Nu}[\text{D}])}[\text{Nu}]. \quad (2)$$

The micellar surface also behaves as a selective ion exchanger, and competition between reactive (Nu) and inert (X) counterions can be expressed as in Eq. (3), in which an empirical ion exchange constant, K_x^{Nu}, accounts both for ionic and hydrophobic contributions to the binding

$$X_m^- + Nu_w \overset{K_x^{Nu}}{\rightleftharpoons} Nu_m + X_w^-. \quad (3)$$

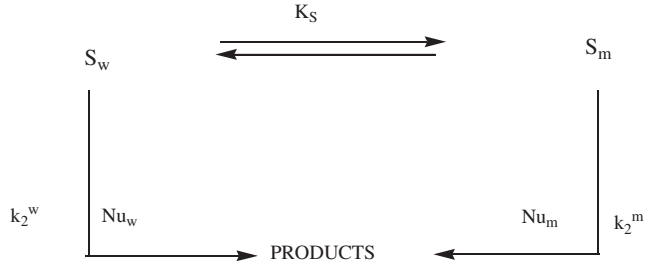


Fig. 5. Partitioning of the reactants between water and micellar pseudophase.

This extension of the pseudophase model has been called the pseudophase ion exchange model or PIE and successfully fits the kinetics of many bimolecular reactions in micellar solutions. In the PIE model, β (the degree of counterion association to the micellar surface) is assumed to be constant and insensitive to surfactant and salt concentrations. Thus, micellar catalysis is still a potential interest for the design and construction of efficient and novel artificial hydrolases.

It is worth noting here that the term "catalysis" was recognized as not absolutely correct since the surfactants are generally not consumed in the reaction. The observed rate constant of nucleophilic attack depends on the partitioning of both nucleophile and electron-deficient substrate between the micelle and the bulk water phase, and it is the "trivial" concentration effect that is responsible for the increasing observed reaction rates. Within the Berezin's approach, the maximum effect is supposed to be observed at the concentration of the micellized surfactant $[D] = 1/\sqrt{K_S K_{Nu}}$ followed by descending of the concentration profile with increase in the surfactant concentration. The phenomenon of "micellar catalysis" was elegantly called by Bunton "a useful misnomer" [52] so researchers currently use less controversial terms such as "micellar rate enhancement" or "micellar effect".

6. Nucleophilicity of oximate ions in water and cationic micelles

Oximate ions are among the most powerful nucleophiles due to the so called α-effect, or supernucleophilicity characterized by a positive deviation from the Bronsted plot for the regular oxygen nucleophiles [58]. Efforts are being made by scientists in order to design more potent reagents for the environmentally benign detoxification of organophosphorus pollutants [59–60], and nucleophilic reactivity of oximate ions has attracted specific interest since the 1950s because some potent efficient cholinesterase reactivators (antidotes) as representatives of this unique class of nucleophiles have been found [61]. The antidotal activity of oximes seems to be directly originated from their anomalously high reactivity. Therefore, an important problem was to elucidate factors governing the α-effect of oximate ions, and it was pointed out that the unfavorable solvation effects are among the main factors governing the nucleophilic reactivity of oximate ions as typical α-nucleophiles [62,63]. It's worth noting that the Bronsted plot for oximate ions undergoes leveling-off at pK_a ca. 9.0, regardless of the nature of the reaction center and leaving group, whereas alkoxide ions demonstrate similar behavior at pK_a ca. 12.5–13.5 [36,60,62]. Thus, oximate ions with pKa >9.0 (β_N is ca. 0.1) undergo negative deviation from the Bronsted plot for oximate ions having low basicity (β_N is ca. 0.5–0.6) and are of the comparable reactivity as alkoxides having $pK_a > 12.5$. Comprehensive analysis of their reactivities [60,62] makes them promising precursors of functionalized surfactants.

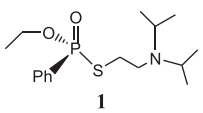
Contributions of Buncel and co-workers [63a,b] deserve a special mention in this context as they have studied degradation of pesticide Fenitrothion using an oxime α-nucleophile i.e. antipyruvaldehyde-1-oxime (monoisonitrosoacetone: MINA) in the presence of cationic surfactants. Substrate orientation within the micelle was clearly manifested in their work. Changes in reactivity and mechanistic pathways under micellar influence have been discussed in detail. Similar approach was made by Buncel and research team [63c] to study micellar accelerated degradation of Fenitrothion in solutions and soils. Tolluec et al. [64a] examined phosphate triester hydrolysis catalyzed by micelles of hexadecyltrimethylammonium anti-pyruvaldehyde-1-oximate. Phosphorolytic reactivity of highly efficient systems based

on *o*-iodosylcarboxylates and related nucleophiles was reviewed by Moss et al. [64b].

Significant studies on nucleophilicity of oximate ions in cationic micelles have been carried out. Bunton et al. [50] demonstrated oximate ion mediated dephosphorylation and deacylation reactions in cationic micelles of cetyltrimethylammonium bromide (CTAB). Recently, Churchill et al. [2c] have published an excellent review on the destruction and detection of chemical warfare agents, along with the history of pesticides, molecular structures and their toxicology. There has been great interest in the studies of quaternary and tertiary pyridinium oximes as α-nucleophiles for the hydrolysis of organophosphorus nerve agents and their application to the reactivation of phosphorylated acetylcholinesterase [17]. Studies demonstrate that the cationic micelles are usually found to invoke no change in mechanism from the reaction in water alone so that alpha effect continues to persist in the micelles which open a way for designing micellar α-nucleophilic systems.

Terrier et al. [36] have carried out a study of NPA hydrolysis with oximate ions, going from water to various H_2O–Me_2SO mixtures of increasing Me_2SO content. The leveling off in the reactivity was seen in water in 70:30 (v/v) H_2O–Me_2SO, but a complete change in behavior occurred in Me_2SO-rich solutions where the linearity of the Brønsted correlation was restored over the whole range of oximate basicity studied and hence, it was suggested that the origin of the observed saturation of reactivity of oximates could arise from a special need for partial desolvation of these species prior to nucleophilic attack that became energetically more costly with increasing basicity. Extending this investigation (leveling of behavior at carbon centers) towards other electrophilic centers, in particular phosphorus centers, they [60] studied potentiometric determination of the pK_a values of oxime (R_1R_2)C═NOH functionality, the second order rate constants (k_{Ox}) for reaction oximate bases (Ox^-, OxH^-, $Ox^=$ derived from the ionization of monoxime, OxH and dioxime, OxH_2) with two model organophosphorus esters, i.e. bis-(4-nitrophenyl)phenylphosphonate (BNPPP) and bis-(4-nitrophenyl)methylphosphonate (BNPMP), and three toxic compounds, i.e., sarin (GB), soman (GD) and diisopropylphosphorofluoridate (DFP), in aqueous as well as a 30:70 (v/v) H_2O–Me_2SO mixture was studied. The corresponding Bronsted-type nucleophilicity plots of log k_{Ox} vs. p$K_{a\ Ox}$ revealed a clear tendency of the reactivity of the oximates to undergo leveling-off with increasing basicity in aqueous solution. In the case of BNPMP and the three toxic esters, this behavior was reflected in a leveling off at p*K*a ≈ 9 but in the BNPPP system the attainment of maximum reactivity at p*K*a ≈ 9 was followed by a clear decrease in rate at higher p*K*a's. This phenomenon is attributed to a "solvational imbalance" caused by the necessity of nucleophile desolvation prior to the nucleophilic attack and is critically important for more basic oximate anions.

Renard et al. [12] have shown remarkable effort to study a series of α-nucleophiles including oximes, amidoximes and hydroxamic functions for degradation of organophosphorus nerve agent, phosphonothioate; PhX (**1**) (an aromatic derivative of VX, see Fig. 3). They have summarized the results of PhX hydrolysis with benzaldoximes, ortho-hydroxybenzaldoximes and amidoximes in the presence of 1 equiv of PhX in 0.1 N Tris/HCl buffer at pH 8.5 and at 20–22 °C.



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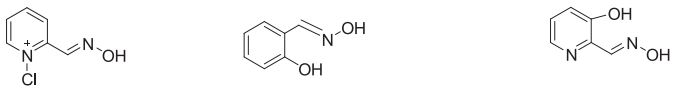
The uncharged nucleophiles, such as oximes and amidoximes showed a comparable and in some cases increased reactivity towards PhX hydrolysis in comparison with 2-pralidoxime **2**. They identified the positive ortho-hydroxyl effect of aryl- and pyridylbenzaldoximes on their hydrolytic activity towards PhX hydrolysis. Pyridinealdoxime **3** (pK_a = 8.2 ± 0.09) bearing OH function in *ortho*-position exhibited significantly higher hydrolytic activity. Further influence of the nature of the other substituents in the aromatic ring of *ortho*-hydroxybenzaldoximes was studied. Benzaldoximes substituted with halogen atoms showed slightly higher to better hydrolytic activities than non-substituted ortho-hydroxyloxime. It was also observed that oximes bearing halogen atom in *para*-position position to the hydroxyl group showed higher organo-phosphono-thioase activity than *ortho*-substituted ones. Inspired by the results obtained for aryl- and pyridylaldoximes series the influence of *ortho*-hydroxyl group and the pyridine ring onto the hydrolytic activity of amidoximes was evaluated. It was discovered that, as observed for arylaldoxime **4** and amidoxime **5** (pK_a = 8.88 ± 0.6,) bearing hydroxyl group in ortho-position to the nucleophilic function, has a significantly higher hydrolytic towards PhX than nonsubstituted compound. Identically, ortho-hydroxylsubstituted amidoximes **6** and **7** bearing an additional hydroxyl group showed a dramatic increase of the organo-phosphono-thioase activity (due to intramolecular H-bonding between amidoxime and OH group). Overall, the α-hydroxybenzalamidoximes showed superior reactivity towards PhX than α-hydroxybenzaldoximes.



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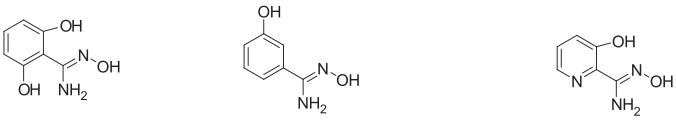
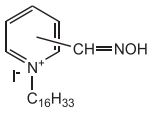
3 **4**



5 **6** **7**

The comparison of PhX hydrolysis results obtained for aldoximes and amidoximes species indicated that in all the cases amidoximes (**5**, **6**, **7**) exhibit higher activity than aldoximes (**3**,**4**) with a similar structure.

We have studied hydrolysis of carboxylate and phosphate esters with mono-pyridinium oximes (**8**), in mixed micelles with cationic surfactants of same hydrophobic chain length (C_{16}) at pH 8.0 (NPA) and 9.0 (NPDPP) [65]. The observed rate constant (k_{obs}) increases with increasing surfactant concentration culminating into a maximum, and this has been analyzed in detail following the concepts of micellar catalysis. The structure activity relationship of the investigated oximes has been discussed, and 2-PAM derivative was found to be the most reactive among all the three investigated oximes for the cleavage of NPA. 4-PAM derivative was the most reactive oxime for the hydrolysis of phosphate ester.



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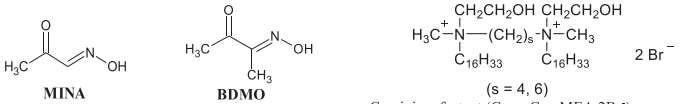
Similar investigations were carried out by our team [66] with tertiary oximes (**9**,**10**) (monoisonitroso acetone; MINA and butane-2,3-dione monooxime; BDMO) for the degradation of carboxylate (*p*-nitrophenyl acetate, NPA and p-nitrophenyl benzoate, NPB), phosphate (*p*-nitrophenyl diphenyl phosphate, NPDPP and bis (2,4-dinitrophenyl) phosphate, BDNPP) and sulfonate (*p*-nitrophenyl p-toluene sulfonate, NPOTos) esters in gemini surfactants (**11**). The first-order rate constant versus surfactant profiles showed micelle-assisted bimolecular reactions involving interfacial ion exchange between bulk aqueous media and micellar pseudophase. It was concluded that MINA exhibited better nucleophilic activity towards ester cleavage than BDMO. Micellar second-order rate constants and binding constants were discussed on the basis of pseudophase model. Acid dissociation constant, pK_a in the absence of gemini was determined as 8.4 and 9.5 for

MINA and BDMO, respectively whereas in the presence of gemini, pK_a was 8.1 and 9.1 for MINA and BDMO, respectively.



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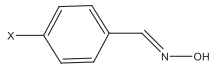
Picha et al. [67] have synthesized a series of *p*-substituted benzaldoximes **12** (*p*-$XC_6H_4CH{=}NOH$, where X = H, CH_3, CF_3, F, Cl, Br, OCH_3, $N(CH_3)_2$, $COOCH_3$, CN, NO_2) and determined their dissociation constants in 10% (v/v) aqueous dioxane at 35 °C.



X	H	CH_3	CF_3	F	Cl	Br	OCH_3	$N(CH_3)_2$	$COOCH_3$	CN	NO_2
pK_a	11.01	11.05	10.51	10.96	10.66	10.79	11.16	11.56	10.48	10.27	10.28

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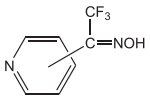
The pseudo-first order rate constants k_{obs}, of their reactions with PNPA were measured at pH values from 7.8 to 10.8 and at concentrations $[Ox]_0$ ranging from 0 to 4 mM. The kinetic model and mechanism of the reaction was proposed by means of mathematical statistical modeling of the dependences of k_{obs} on pH and $[Ox]_0$. The suggested mechanism of the reaction of the oximate ions at tetrahedral carbon atom involved a pre-equilibrium (k_{-1}/k_1) in which PNPA formed a tetrahedral intermediate (THI) with the deprotonated form of oxime. In the given medium, THI was shown to be in equilibrium with the non-reactive conjugated acid THIH (pK_a,THIH) which was stabilized by intramolecular hydrogen bond. Depending on pH, the rate-limiting step consists either in formation of THI from educts (pH < pK_a,oxime) or in its spontaneous (k_2) and oxime-catalyzed (k_3, general acid catalysis) decomposition to products (pH > pK_a,oxime). Evaluation of substituent effects on dissociation constants of the oximes showed that there is no direct conjugation between the substituent and the reaction center. The transmission coefficient of the transfer of these effects through C═N—O grouping corresponded approximately to one bond. Applying regression model, the obtained reaction constants from Hammett equation were: $\rho(k_{-1}K_a,\text{THIH}/k_1) = 1.29$, $\rho(k_2K_a,\text{THIH}) = 0.20$ and $\rho(k_3K_a,\text{THIH}) = 0.67$.

Salvador et al. [68] have synthesized 2-, 3-, and 4-trifluoromethyl ketoxime isomers (**13**) of pyridine and N,N-dimethylaniline. They found that these nucleophiles were quite active in providing protection against either paraoxon or sarin. In spite of the moderate their antidotal activity, high reactivity of these compounds is due to the inductive effect of the CF_3 group.



13

The inductive effect of the CF_3 group is sufficient to bring the pK_a value of the oximes in the range for maximal reactivation properties and could be considered as a precursor of the low basicity oxime functionalized surfactant.

7. Functionalized oximes: bringing together micellar effect and enhanced reactivity

Modern approaches include the design of active components for fast and irreversible decomposition of ecotoxicants. For instance, the micellar effects of surfactants in the reactions of anionic nucleophiles may be applied to design organized molecular systems which would cleave highly toxic OPCs, esters and acid halides of phosphorus acids. The most efficient micellar systems would be and are those combining the advantages of microheterogenic environment characterized by a high solubilizing ability with respect to the substrate and of inorganic anionic α-nucleophile characterized by an abnormally high reactivity with respect to the electron-deficient sites (phosphorus, sulfur, and carbon atoms). One of the most promising ways of modification of cationic surfactant molecules include the introduction of functional groups into the head part capable of forming highly reactive anionic species, e.g., specific nucleophilic fragments [69,70]. These nucleophilic groups in the so-called functional cationic tensides are activated by the electron withdrawing effect of the polar head group and can be easily deprotonated to form powerful nucleophile attacking the ester bond. As for hydrolysis reaction, normally, functionalized surfactants were proved to be active due to the formation of alpha nucleophile originated from functional group present in the molecule. In addition, micelles can provide hydrophobic environment, which facilitate the increase in local concentration of substrate. Owing to the polar interaction or electrostatic attraction between reactive molecules and micelle aggregates, chemical reactions are probably accelerated. In most of the cases, formation of micelle aggregates can promote reactions compared to the other systems without the addition of surfactants [71]. The immediate advantage of functional surfactants is the maximum possible local concentration of α-nucleophile fragment which is reached at any micelle concentration and the highest rates are observed for the most hydrophobic esters. Because of that, many efforts of the researcher in the field are directed towards development of novel functionalized surfactants [72–75]. Reactivities of some oxime-functionalized surfactants towards different substrates and the half-lives of these substrates under similar reaction conditions are summarized in Table 1.

To estimate nucleophilicities of the functionalized surfactants, Eq. (2) can be modified towards Eq. (4):

$$k_\psi = \frac{k'_w + \left(k_2^m / V_m\right) K_s[M]}{(1 + K_s[M])} \tag{4}$$

demonstrating rate-concentration profile with the saturation that can be characterized by the limit observer rate constant value k_{max} corresponding to the complete binding of the substrate to micelle.

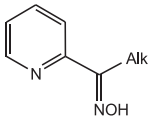
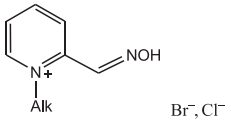
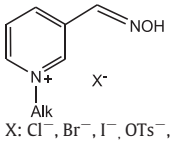
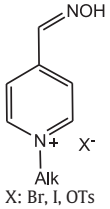
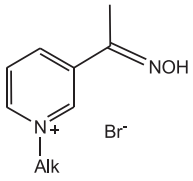
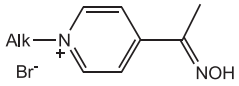
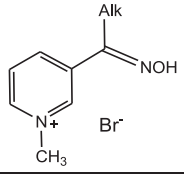
Taking into account the principles of the PPM approach, the Eq. (5) can be proposed to estimate the main factors responsible for the micellar rate effect of the functionalized surfactants [76].

$$\Delta = \Delta_1 \cdot \Delta_2 \cdot \Delta_3 = \frac{k_2^m}{k_2^w} \cdot \frac{K_s[D]}{V_M \cdot [Ox]_{0,w} \cdot (1 + K_s[D])} \cdot \frac{K_{a,app}(K_a + a_{H^+})}{K_a\left(K_{a,app} + a_{H^+}\right)}. \tag{5}$$

In Eq. (5), Δ_1 corresponds to intrinsic change in nucleophilicity of functionalized oximate surfactant and its nonmicellized short-chain (usually methyl) analog with the same structure of reactive center; Δ_2 reflects a "trivial" concentration effect owing to solubilization of a substrate, Δ_3 indicates the $pK_{a,app}$ shift of the nucleophic center in the micellar pseudophase. It is widely thought that the nucleophilicity generally does not change critically to have k_2^m values comparable or lower than the reactivity of its methyl derivative in water.

At the same time, the Δ_2 value dependent on the partitioning coefficient of the substrate and a micelle is responsible for abnormal increasing of the observed reaction rates up to several orders of magnitude. Since the oxime acts as nucleophile in its deprotonated form, the Δ_3 factor plays a role in the case if the deprotonation is incomplete, or if cationic component is sufficient in the mixed micelle

Table 1
Reactivity of oxime-functionalized surfactants towards different substrates.

	Structure	Alk	Substrate	pH	D_t, mM	k_{obs}, s^{-1}	$\tau_{1/2}$, s
Pyridinium/pyridine head group							
1		$C_{12}H_{25}$ [94]	NPDPP	10.0	0.33	$3.2 \cdot 10^{-3}$	220
2	 Br^-, Cl^-	$C_{16}H_{33}$ [81]	NPDEP	10.0	0.7	$2.4 \cdot 10^{-3}$	290
		$C_{14}H_{25}$ [94]	NPDPP	10.0	0.33	$3.2 \cdot 10^{-3}$	220
3	 X: Cl^-, Br^-, I^-, OTs^-, OMs^-	$C_{10}H_{21}$ [86]	NPDPP	9.0	5.0	$1.29 \cdot 10^{-3}$	537
		$C_{10}H_{21}$ [86]	BDNPP	9.0	5.0	$0.9 \cdot 10^{-4}$	7700
		$C_{10}H_{21}$ [86]	NPOTos	9.0	5.0	$0.3 \cdot 10^{-4}$	23,100
		$C_{12}H_{25}$ [86]	NPDPP	9.0	5.0	$2.78 \cdot 10^{-3}$	250
		$C_{12}H_{25}$ [86]	BDNPP	9.0	5.0	$5.0 \cdot 10^{-4}$	1390
		$C_{12}H_{25}$ [86]	NPOTos	9.0	5.0	$1.4 \cdot 10^{-4}$	4950
		$C_{12}H_{25}$	PNPA	9.0	3.0	$28.4 \cdot 10^{-3}$	–
		$C_{14}H_{29}$ [86]	NPDPP	9.0	5.0	$9.07 \cdot 10^{-3}$	76
		$C_{14}H_{29}$ [86]	BDNPP	9.0	5.0	$3.38 \cdot 10^{-3}$	205
		$C_{14}H_{29}$ [86]	NPOTos	9.0	5.0	$2.59 \cdot 10^{-3}$	270
		$C_{16}H_{33}$ [86]	BDNPP	9.0	5.0	$16.2 \cdot 10^{-3}$	42
		$C_{16}H_{33}$ [86]	NPOTos	9.0	5.0	$5.77 \cdot 10^{-3}$	120
		$C_{16}H_{33}$ [86]	NPDPP	9.0	5.0	$4.10 \cdot 10^{-3}$	170
		$C_{12}H_{25}$ [48]	NPDEP	10.6	2.0	$1.27 \cdot 10^{-3}$	545
		$C_{14}H_{25}$ [94]	NPDPP	10.0	0.33	0.14	5
		$C_{16}H_{33}$ [84]	NPDEP	10.5	0.6	$8.0 \cdot 10^{-3}$	87
4	 X: Br, I, OTs	C_6H_{13} [79,80]	DFP	10.0	60	$7.5 \cdot 10^{-4}$	925
		C_8H_{17} [79,80]	DFP	10.0	60	$7.2 \cdot 10^{-3}$	96
		$C_{12}H_{25}$ [79,80]	DFP	10.0	60	$5.3 \cdot 10^{-3}$	130
		$C_{16}H_{33}$ [79,80]	DFP	10.0	60	$2.6 \cdot 10^{-3}$	266
		C_6H_{13} [95]	NPDEP	10.0	1.5	$8.4 \cdot 10^{-4}$	825
		C_8H_{17} [95]	NPDEP	10.0	1.6	$1.1 \cdot 10^{-3}$	630
		$C_{10}H_{21}$ [86]	NPDPP	9.0	5.0	$2.55 \cdot 10^{-3}$	270
		$C_{10}H_{21}$ [86]	BDNPP	9.0	5.0	$1.08 \cdot 10^{-3}$	640
		$C_{10}H_{21}$ [86]	NPOTos	9.0	5.0	$0.91 \cdot 10^{-3}$	760
		$C_{12}H_{25}$ [95] (Br^-, I^-, OTs^-)	NPDEP	10.0	0.7	$7.2 \cdot 10^{-4}$	960
		$C_{12}H_{25}$ [86]	NPDPP	9.0	5.0	$4.34 \cdot 10^{-3}$	160
		$C_{12}H_{25}$ [86]	BDNPP	9.0	5.0	$1.63 \cdot 10^{-3}$	425
		$C_{12}H_{25}$ [86]	NPOTos	9.0	5.0	$2.09 \cdot 10^{-3}$	330
		$C_{14}H_{25}$ [84]	NPDPP	10.0	0.33	0.086	8
		$C_{16}H_{33}$ [95]	NPDEP	10.0	0.6	$4.5 \cdot 10^{-3}$	155
5		$C_{12}H_{25}$ [83a]	NPDPP	7.2	4.5	$9.0 \cdot 10^{-3}$	77
		$C_{12}H_{25}$ [89]	NPDEP	10.5	12	$3.74 \cdot 10^{-3}$	190
		$C_{12}H_{25}$ [89]	NPDEPN	10.5	11	0.077	9
		$C_{12}H_{25}$ [89]	NPOTos	10.5	12	0.045	15
		$C_{12}H_{25}$ ($\chi = 0.25$) [89]	NPOTos	10.5	6.0	0.014	50
		$C_{14}H_{29}$ ($\chi = 0.25$) [89]	NPDEP	10.5	6.0	$1.7 \cdot 10^{-3}$	410
		$C_{14}H_{29}$ ($\chi = 0.25$) [89]	NPDEPN	10.5	6.0	0.027	27
		$C_{14}H_{29}$ ($\chi = 0.25$) [89]	NPOTos	10.5	6.0	0.01	70
		$C_{16}H_{33}$ ($\chi = 0.25$) [89]	NPDEP	10.5	6.0	$2.35 \cdot 10^{-3}$	300
		$C_{16}H_{33}$ ($\chi = 0.25$) [89]	NPDEPN	10.5	6.4	0.064	11
		$C_{16}H_{33}$ ($\chi = 0.25$) [89]	NPOTos	10.5	5	0.011	60
6		$C_{12}H_{25}$ [96]	NPDPP	7.2	1.0	$6.7 \cdot 10^{-3}$	105
7		$C_{12}H_{25}$ [83a]	NPDPP	7.2	2.0	0.27	3

(continued on next page)

Table 1 (*continued*)

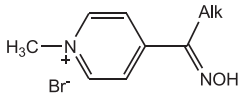
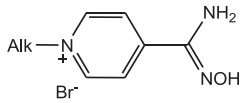
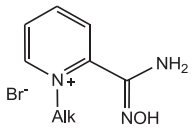
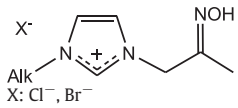
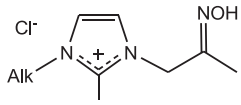
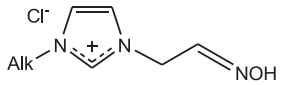
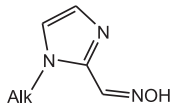
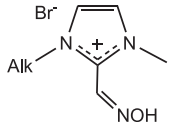
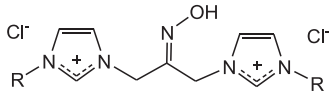
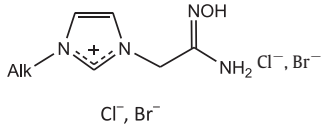
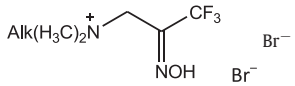
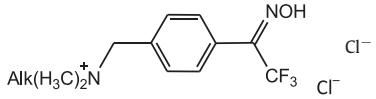
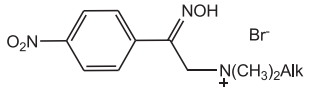
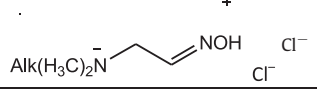
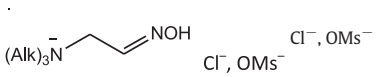
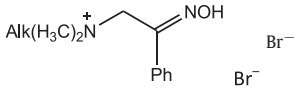
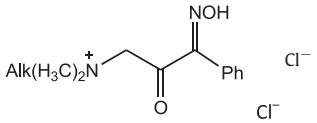
	Structure	Alk	Substrate	pH	D_t, mM	k_{obs}, s^{-1}	$\tau_{1/2}$, s
Pyridinium/pyridine head group							
8		$C_{12}H_{25}$ [96]	NPDPP	7.2	1.0	$5.0 \cdot 10^{-3}$	140
9		$C_{16}H_{33}$ [84]	NPDPP	10.6	0.131	$7 \cdot 10^{-3}$	100
		$C_{12}H_{25}$ [70]	PNPA	9.0	2.0	$0.71 \cdot 10^{-3}$	–
10		$C_{16}H_{33}$ [84]	NPDPP	10.6	0.97	$2.61 \cdot 10^{-2}$	27
Imidazolium/imidazole headgroup							
11		$C_{12}H_{25}$ [89,90]	NPOTos	10.5	5	0.023	30
		$C_{12}H_{25}$ [89,90]	NPDEP	10.5	1.06	$3.7 \cdot 10^{-3}$	190
		$C_{12}H_{25}$ [89,90]	NPDEPN	10.5	9.5	0.053	13
		$C_{14}H_{29}$ [89,90]	NPOTos	10.40	20	0.032	22
		$C_{14}H_{29}$ [89,90]	NPDEP	10.45	40	0.01	70
		$C_{14}H_{29}$ [89,90]	NPDEPN	11.40	3.8	0.13	5
		$C_{16}H_{33}$ [91]	NPOTos	12.9	21	$6.1 \cdot 10^{-2}$	12
		$C_{16}H_{33}$ [91]	NPDEP	12.9	50	$1.6 \cdot 10^{-2}$	43
		$C_{16}H_{33}$ [91]	NPDEPN	12.6	50	$30 \cdot 10^{-2}$	3
12		$C_{16}H_{33}$ [76]	NPDEP	–	–	–	53
			NPDEPN				1
			NPOTos				9
13		$C_{16}H_{33}$ [91e]	NPDEP	–	–	–	14
			NPDEPN				2
			NPOTos				9
14		$C_{14}H_{29}$ [84]	NPDPP	10.0	0.33	0.5	1.4
			NPDETP	10.0	0.33	$6.81 \cdot 10^{-4}$	1018
15		$C_{12}H_{25}$ [87b]	NPDEP	10.5	20	0.022	32
		$C_{14}H_{29}$ [87b]	NPDEP	10.5	10	0.021	33
		$C_{16}H_{33}$ ($\chi = 0.25$) [87a]	NPDEP	9.30	6.0*a*	0.0045	153
		$C_{16}H_{33}$ ($\chi = 0.25$) [87a]	NPDEPN	9.30	6.0*a*	0.063	11
		$C_{16}H_{33}$ ($\chi = 0.25$) [87a]	NPOTos	9.30	6.0*a*	0.0088	79
16		$C_{12}H_{25}$ [95]	NPDEP	10.94	1.34	0.014	50
		$C_{12}H_{25}$ [95]	NPDEPN	10.0	1.03	0.045	15
		$C_{12}H_{25}$ [95]	NPOTos	11.0	1.03	0.020	35
		$C_{14}H_{29}$ [95]	NPDEP	N/A	12.5	0.032*b*	22
		$C_{14}H_{29}$ [95]	NPDEPN	N/A	6	0.36*b*	2
		$C_{14}H_{29}$ [95]	NPOTos	10.5	5	0.035*b*	20
		$C_{16}H_{33}$ [95]	NPDEP	N/A	4	0.025*b*	28
		$C_{16}H_{33}$ [95]	NPDEPN	N/A	2	0.25*b*	3
		$C_{16}H_{33}$ [95]	NPOTos	N/A	2	0.04	17
17		$C_{16}H_{33}$ [91]	NPDEP	13.5	15	0.019	37
		$C_{16}H_{33}$ [91]	NPDEPN	13.5	15	0.35	2
		$C_{16}H_{33}$ [91]	NPOTos	13.5	15	0.087	8
Tetraalkylammonium head group							
18		$C_{12}H_{25}$ [79,80]	DFP	10.0	60	$2.8 \cdot 10^{-4}$	2480
19		$C_{12}H_{25}$ [79,80]	DFP	10.0	60	$1.2 \cdot 10^{-4}$	5940
20		$C_{14}H_{29}$ [84]	NPDPP	10.0	0.33	0.134	5.2
			NPDETP	10.0	0.33	$2.53 \cdot 10^{-5}$	27,390
−21		$C_{16}H_{33}$ [77]	NPDPP	11.7	2.0	3.2	0.2
			NPB	11.7	2.0	17	0.04

Table 1 (*continued*)

	Structure	Alk	Substrate	pH	D_t, mM	k_{obs}, s^{-1}	$\tau_{1/2}$, s
Tetraalkylammonium head group							
22		C_8H_{17} [77]	NPDPP	11.7	0.35	0.1	6.9
			NPB	11.7	0.6	0.62	1.1
23		$C_{12}H_{25}$ [50]	NPDPP	12.0	1.5	0.4	1.7
24		$C_{12}H_{25}$ [78]	NPA	7.95	1.5	2.6	0.27

Note: *a*—Total concentration of mixed surfactant system; *b*—calculated from k_{obsd}/α_{Ox}.

with deprotonated oximate-functionalized surfactant (usually zwitterionic). Therefore, Δ has it nominally maximum value in that limiting case if the substrate binding to a micelle is incomplete ($K_S[D] << 1$), and $pK_{a,app}$ shift is sufficient, see Eq. (5) [76]

$$\Delta = \frac{k_2^m}{k_2^w} \cdot P_S \cdot \frac{K_{a.app}}{K_a}. \quad (5)$$

It should be noted that in contrast to the condition when nominally high values of the micellar rate effects, k_ψ^m/k_ψ^w, can be reached, the fast observed cleavage of the substrate (high k_ψ, s^{-1}, or low $\tau_{1/2}$, see Table 1) requires (i) sufficient fraction of bound substrate (i.e. $K_S[D]/(1+K_S[D]) \rightarrow 1$) and (ii) complete or nearly complete deprotonation degree of the oximate ion.

Bunton et al. [50] have studied the comicelles of dodecyl [2-(hydroximino)-2-phenylethyl]dimethylammonium bromide with CTABr towards the dephosphorylation of *p*-nitrophenyldiphenyl phosphate (NPDPP) at high pH showing deprotonation of oxime to oximate ions. Comparison of the rate constants in the comicelles with those for reactions in water, with monomeric oximate by deprotonation of the oxime showed that the second-order rate constants in the micellar pseudophase were very similar to those in water. The rate constants and reaction mechanism in micellar and aqueous pseudophases were discussed on the basis of substrate hydrophobicity.

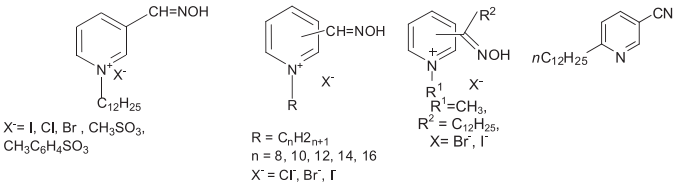
Alkoxides were synthesized by Bunton and Biresaw [77] to study the size versus reactivity of functionalized assemblies for deacylation and dephosphorylation reactions. In order to obtain more reactive systems, oxime functionalized aggregates with tetra alkylammonium head group were investigated by Tonellato [78] and coworkers. They observed large rate enhancements for nucleophilic substitution reactions using these functionalized assemblies and concluded that the rate acceleration was mainly due to concentration effects whereas the nucleophilicity of oximate ions did not change critically. DFP hydrolysis was studied by Reiner and Rossmann [79,80] with the aid of oxime functionalized aggregates at pH 10.0.

Lion et al. [81] have studied hydrolysis of Paraoxon (NPDEP) with *N*-alkyl hydroximinomethylpyridinium salts. The high reactivity of oximate ions was associated with micelle forming molecules. The position of the hydroximinomethyl function (ortho, meta or para), the length of the alkyl chain and the nature of the anion were discussed.

The problem of high basicity and therefore insufficient environmentally friendliness of the alkoxy moiety of above functionalized surfactants makes them less attractive decontaminants that surfactants bearing specific fragment of α-nucleophile, first of all, oximes. Pyridinium based functionalized surfactants widely used for detoxification of organophosphorus compounds and nerve agents also demonstrate direct pharmacological effects [82].

8. Pyridinium based oxime functionalized surfactants

Epstein et al. [48] have systematically studied the micellar behavior of 1-*n*-dodecyl-3-(hydroxyiminomethyl) pyridinium salts against two neutral organophosphates, paraoxon and VX. Hampl and co-workers [83] have synthesized several amphiphilic quaternary pyridinium ketoximes (**14**) comicellized with CTAB and have examined their efficiency for hydrolysis of *p*-nitrophenyldiphenyl phosphate and other simulants of organophosphates.



$R^1=CH_3$, $R^2 = C_{12}H_{25}$, X= Br^- $R^1=CH_3$, $R^2 = C_nH_{2n+1}$ (n=8-16)

17

They found that the nucleophilicity of the deprotonated hydroxyimino group in these functional surfactants depends on its position relative to micellar surface. Series of micellar hydrolytic pyridine ketoximes (**15**) were prepared and 2- and 4-[(hydroxyimino)tridecyl]-1-methylpyridinium bromides were surprisingly the most effective. The head group orientation of functionalized surfactants at micellar/water interface (see Fig. 6) can play a crucial role for the reaction volume of the functional micelle.

Besides good yields of pyridinium ketoximes, 6-dodecylpyridine-3-carbonitrile (**16**) has been obtained. An efficient method for the synthesis

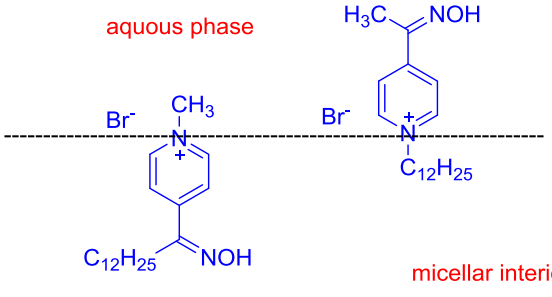
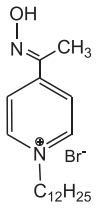


Fig. 6. Orientation of functionalized surfactants at micelle/water interface.

of *N*-[2-hydroxyimino-2-(pyridin-2-yl-ethyl)]-dialkylmethylammonium and *N*-[2-oxo-2-(pyridin-2-yl-ethyl)]-dialkylmethylammonium lipophilic salts (**17**) was reported and these compounds were used for metal ion extraction from aqueous solutions into organic solvents [83c].



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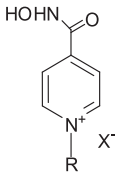


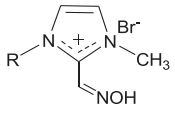
19

The research team of Prokop'eva et al. [84] has studied the head group modification by preparing pyridine functional detergents with aldoximes (**14**), ketoxime (**18**) and hydroxamate (**19**) functional groups. Comparative study of their reactivity in cationic surfactants (as comicelles) for cleavage of NPDEP and NPTos was carried. Hydroxamate functional detergents showed the lowest basicity ($pK_a = 6.15$) and the highest basicity was observed for the ketoxime group ($pK_a = 8.51$) whereas aldoxime functionalized surfactant showed moderate basicity ($pK_a = 7.92$).

Since last few years, our research group has been engaged in physicochemical and kinetic studies of various oximes and oxime based functionalized surfactants for the hydrolysis of carboxylate, phosphate and sulfonate esters [45,65,66,85,86].

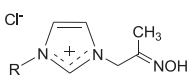
9. Imidazolium based oxime functionalized surfactants

In contrast to the pyridinium derivatives, oxime surfactants with imidazolium headgroups are reported to have lower Krafft temperature and therefore have better solubility in water under reaction conditions. Recently, Kapitanov et al. [87] studied nucleophilicity of oximate fragment from amphiphilic derivatives of 2-(oximinomethyl)imidazole surfactants (**20**) in mixed micelles with CTABr used to examine cleavage of 4-nitrophenyl diethyl phosphate (NPDEP) and phosphonate (NPDEPN).

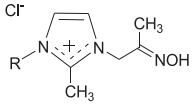


20

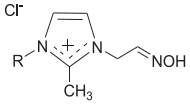
Hydrophobic properties of imidazolium functional surfactants of the type 1-alkyl-3-(2-oximinopropyl) imidazolium chloride **21** for cleavage of environmental toxicants were also documented by this team (Prokop'eva and coworkers) [88–91].



21a

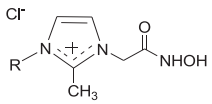


21b

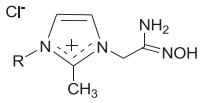


21c

The reactivity of co-micelles of functional surfactants (**21**–**23**) with cationic surfactants towards the hydrolysis of organophosphorous (NPDEP and NPDEPN) and sulphonate (NPOTos) esters was investigated by one of us [91e,g]. It was shown that the nucleophilicity of the functional groups in the surfactant does not undergo substantial changes with variation in the nature of the head group of the cationic surfactant and the fraction of functional detergent in the co-micelle. Simanenko et al. [76, 91a,b] performed a detailed kinetic analysis of nucleophilic cleavage of some phosphate (prosphonate) and sulfur esters. The cleavage kinetics in micelles of functional detergents and combined micelles of functional detergents with cetyltrimethylammonium chlorides are adequately described in the simple framework of pseudophase partitioning model.



22

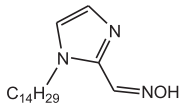


23

The reactivities of the imidazolium and pyridinium surfactants bearing oxime moiety have been analyzed using the Bronsted plots [76, 92] to demonstrate non-linearity similar to those observed in the case of non-micellizing oximes.

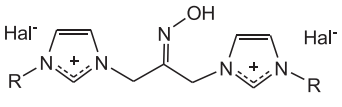
Amidoximate ions (e.g. **5**–**7**, **20**) form a distinct class of the organic α-nucleophiles with nucleophilic reactivities comparable to that of oximate ions. The α-effect decreased with the growing basicity of amidoximate ions, and for compounds with $pK_a > 12.0$ it totally disappears [93]. At the same time, amidoximes demonstrate high nucleophilic activity of both neutral and anionic forms ascribed to the cyclic structure of the transition state involving general acidic and basic catalysis. A unique feature of amidoximes as nucleophiles consists in their ability to perform efficient cleavage of substrates in a wide pH range, from basic to acid media. The amidoximate functionalized surfactants provides abnormally high rate effects mostly at very high pH which makes them less preferable components for mild decontamination systems then oximate surfactants.

Dai et al. [94] designed and synthesized a long-chain oxime *N*-tetradecylimidazole-2-aldoxime **24**. The reactivities of this and other long-chain oximes with NPDPP, *p*-nitrophenyl diethyl thiophosphate (parathion), and O-ethyl (s-β-diisopropylaminoethyl) emthyl phosphonothiolate (VX) were studied. The results showed that **20** was a powerful nucleophile that was 5–10 times more active than those oximes reported so far and was useful in non-corrosive decontamination of stable and toxic phosphate esters.



24

Recently, Kapitanov et al. [95] has reported the synthesis of some new functionalized gemini surfactants to study the decomposition of 4-nitrophenyl esters derived from phosphorus and sulfur acids. A series of imidazolium based gemini surfactants with variable chain lengths **25** have been recently reported by the Ukrainian team to demonstrate fitting the Bronsted plot for oximate functionalized (monomeric) surfactants [92] alone with high solubilization power and anomalously low cmc values (Fig. 7). The undoubted advantage of dimeric surfactants is their especially low critical micelle concentrations (≤0.01 mM), providing a possibility to attain the same micellar effects at the surfactant concentration lower by an order of magnitude and even lower than in the case of monomeric analogs.

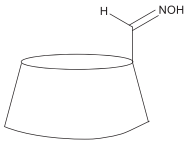


25

10. Reactive polymers bearing oxime moiety

Polymers that are functionalized with reactive nucleophiles have been studied widely as hydrolysis reagents and catalysts [97]. These

when attached to a highly nucleophilic group can result in increased reactivity towards phenyl esters relative to their non-functionalized form. Czarnik et al. [98] have reported the synthesis of β-cyclodextrin (β-CD) oxime by the covalent attachment of oxime onto the 1°- and 2°-sides of β-CD (**26**, **27**). This class of β-CD oxime provided high nucleophilicity, given their combination of α-effect and relative acidity (pK_a). However, the oxime functional group was not incorporated onto a cyclodextrin. The secondary-side derivative was converted to the first secondary-side keto-cyclodextrin.

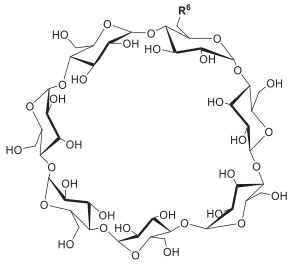


26: 1°-side β –cyclodextrin oxime

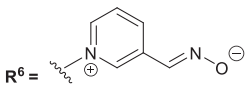
27: 2°-side β –cyclodextrin oxime

They further studied the transacylation of *p*- and *m*-nitropheynyl acetate with β-CD appended with various α-nucleophiles (oxime, hydrazine, hydroperoxide and hydroxylamine) [99]. Although primary side hydroxylamines showed remarkable effects, β-CD oximes were considerably fine. With respect to their potential use as OP scavengers it has been shown that native cyclodextrins accelerate the cleavage of toxic phosphonates, for example sarin and soman [100]. Moreover, modified cyclodextrins containing nucleophilic groups along the cavity have been shown to reduce the inhibitory effect of cyclosarin (GF), paraoxon, and tabun (GA) on AChE by mediating degradation of these OPCs [101].

Zengerle et al. [102a] identified cyclodextrin derivative (**28a**) with an oxime-derived substituent (**28b**) that extremely and efficiently mediates GF decomposition.



28a



28b

The group [102b] also showed that pyridinium-derived substituents with an aldoxime group in 3- or 4-position to a β-CD ring also have a strong effect on the degradation of tabun (GA) at physiological pH. Activity was dependent on the structure, the number, and the position of the substituent on the ring. The highest activity was observed for a β-CD containing a 4-formylpyridinium oxime residue in 6-position of one glucose subunit, which detoxifies tabun with a half-time of 10.2 min. The results provided evidence that the mode of action of the cyclodextrin involves covalent modification of its oxime group rendering the scavenger inactive after reaction with the first tabun molecule.

Andrianov et al. [103] have studied kinetics of reaction between paraoxon and linear and crosslinked hydrolphilic co-polymers carrying aldoxime-or ketoxime functionalities. Along with the nucleophilic properties and basicity of the oxime groups, polymer matrix also contributed to the reactivity of copolymers. Oxime containing polymers catalyzed the decomposition of organophosphate following a first-order kinetics.

Hatton et al. [104a] catalytically hydrolyzed model warfare agent, diisopropyl fluorophosphate, in aqueous media by suspensions of magnetite (Fe_3O_4) nanoparticles modified with poly(1-vinylimidazole-*co*-acrolein oxime-*co*-acrylic acid) (**29**) that acts in an enzyme-like fashion (Fig. 8).

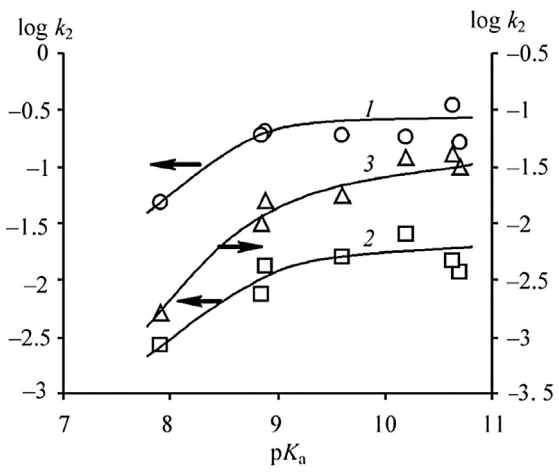
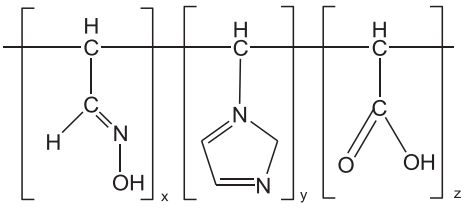


Fig. 7. Bronsted plots for the series of oxime-functionalized surfactants in the reaction towards *p*-nitrophenyl esters of phosphonic *1* (NPDEPN), phosphoric *2* (NPDEP), and 4-toluenesulfonic *3* (NPOTos) acids [92].



29: copolymer p(Vim-AcOx-AA)

The oxime-modified magnetite particle served as a nanosized particulate carrier with nucleophilic groups immobilized on its surface. The oxime-modified magnetite nanoparticles were colloidally stable within a wide pH range and were readily recovered for reuse with no loss of catalytic activity. Because of the positive charge at neutral pH, the novel particles adsorb organophosphoric acids, the products of the nerve agent decomposition, thus affording a one-step water remediation.

This group further studied nucleophilic hydrolysis of chemical warfare agents VX, Soman and Sarin by polyacrylamidoxime (PANOx) and poly(*N*-hydroxyacrylamide) (PHA) [104b]. The reactive PANOx was obtained by one-step oximation of polyacrylonitrile (Fig. 9). The polymer was converted to its respective oximate salt at pH values greater than the p*K*a of the oximate group; 7.5. When exposed to ambient air or 100% humidity, the polymer imbibed up to 65 wt.% water, which dramatically enhanced the polymer reactivity towards the CWA under study. The half-lives of VX in heterogeneous hydrolysis, which appeared to be pseudo-first order in the polymer dispersions, were measured to

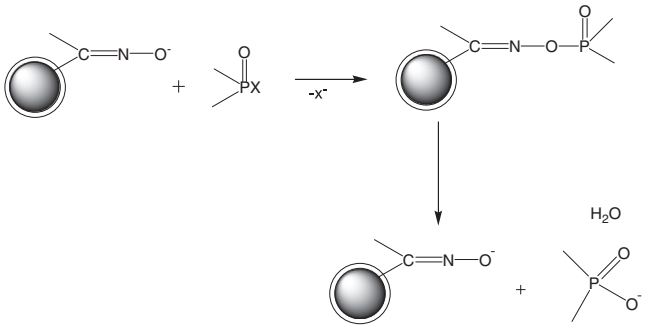


Fig. 8. Hydrolysis of an organophosphate by a nanoparticle-immobilized nucleophile [104].

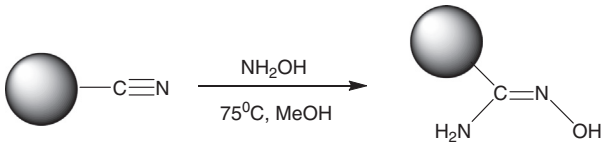
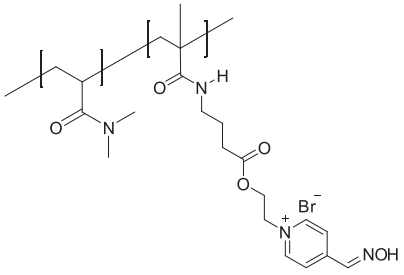


Fig. 9. Reaction of PAN with hydroxylamine (conversion of PAN to PANOx).

be from 0.093 to 4.3 h in the presence of PANOx. The rates of hydrolytic activity of PANOx for VX exhibited a strong dependency on the degree of conversion of the amidoxime to amidoximate groups. The half-life of GB was less than 3 min. Only a minor presence of the toxic VX degradation product, *S*-[2-(diisopropylamino)ethyl]methylphonothioate (EA-2192), was detected in the course of degradation by the reactive polymers. The efficiency, ease of synthesis, and nontoxic nature of the PANOx and PHA polymers made them attractive materials in decontamination and as components of reactive barriers.

Russel et al. [105] reported the decontamination of chemical and biological agent with the aid of polymers based on a dimethylacrylamide-methacrylate (DMAA-MA) copolymer backbone. New materials combining these biopolymers with a family of N-alkyl 4-pyridinium aldoxime (4-PAM) halide-acrylate co-polymers offered both nucleophilic activity for the detoxification of organophosphorus nerve agents and internal sources of halide ions for generation of biocidal activity. Detoxification of diisopropylfluorophosphate (DFP) by the polyDMAA MA-4-PAM iodide component (**30**) was dose-dependent reaching 85% within 30 min. A subset of 4-PAM-halide co-polymers was designed to serve as a controlled release reservoir for N-hydroxyethyl 4-PAM (HE 4-PAM) molecules that reactivate nerve agent-inhibited acetylcholinesterase (AChE). Release rates for HE 4-PAM were consistent with hydrolysis of the HE 4-PAM from the polymer backbone. The HE 4-PAM that was released from the polymer reactivated DFP-inhibited AChE at a similar rate to the oxime antidote 4-PAM.



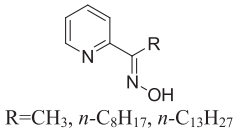
Aglietto et al. [106] documented optically active polymers containing oxime groups prepared: (i) by partial quaternization of poly(4-vinyl pyridine) (P4VP) with phenacyloxime bromide and with (+)-(S)-l-bromo-2-methylbutane; and (ii) by reaction of the copolymer from 4VP and (+)-(S)-5-methyl-l-hepten-3-one with hydroxylamine. These polymers were used as catalysts for the cleavage of *p*-nitrophenol esters with non-chiral and with chiral acids. The kinetic parameters of the catalytic process were clearly dependent on the structure of polymer and substrate.

11. "Noncovalent" functionalization: oxime metallomicelles

The property of oximes to coordinate metal cations can play an important role in affecting reaction rates of esterolysis in the systems containing both oximes and transition metals. As is was recently reported by Yatsimirski [107] Zn(II) and Cd(II) complexes of a tridentate oximate ligand cleave NPA with rate constants being over two orders of magnitude higher than it was reported to be the maximum possible level for highly basic free oximate anions. The metal ions assist in the removal of the "solvational imbalance" of the nucleophile by metal coordination. It was pointed out that the coordination reduces the pK_a of oxime group below 8 and as in a case of organic oximes one observes a Bronsted relationship within groups of complexes with ligands of similar structure. Noteworthy, metal ions catalyze the hydrolysis of *O*-acyl oximes converting oximes from stoichiometric nucleophilic reactants to catalysts.

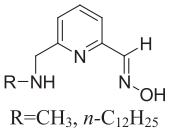
This type of "non-covalent" functionalizations when oximate ions are coordinated with a metal ion (metallomicelles) has also been reported [55, 108]. Colloid particles (micelles, vesicles, or microemulsions) can be doped by reactive functional surfactants commonly known as "metallo-surfactants" [109]. Although metal complex chemistry has achieved a milestone towards hydrolysis of toxic substrates, metal complexes with amphiphilic moieties have proved to be the most efficient system towards the degradation of toxic OPCs and lipophilic substrates like PNPDPP [62]. Cu (II) and Zn (II) coordinated functionalized nano-aggregates have been widely studied towards esterolytic reactions [110].

A series of 2-pyridineketoximes **31a** with different alkyl chain lengths (CH_3, C_8H_{17}, $C_{13}H_{27}$) was synthesized, and their complexes with Cu(II), Co(II), Zn(II), and Ni(II) was investigated towards cleavage of *p*-nitrophenyl esters of carboxylic (NPA and NPH) and phosphoric acids in water or in comicelles with CTAB by Tonellato et al. [111a]. While the Co(II) and Cu(II) complexes were ineffective in promoting the cleavage of PNPA and PNPH esters, the Zn(II) and especially the Ni(II) complexes strongly accelerated the cleavage of such substrates. In case of Ni (II), strong confirmation was obtained concerning the mode of action which involved nucleophilic attack of the oximate ions on the carbonyl carbon of the ester to give, as transient intermediate, the acylated oxime. Unlike carboxylate esters, ketoximes metalloaggregates were ineffective towards the cleavage of NPDPP. In extension to this investigation the authors [111b] introduced a third chelating nitrogen on the ligand in order to have stronger complexes with better defined stoichiometries and synthesized the 2-pyridinealdoxime derivatives **31b** functionalized in the 6 position with an alkylaminomethyl substituent. Ni (II) and Zn (II) complexes of this ligand (**31b**) were investigated towards the NPA and NPH hydrolysis in absence and presence of CTAB micelles.



R=CH_3, *n*-C_8H_{17}, *n*-$C_{13}H_{27}$

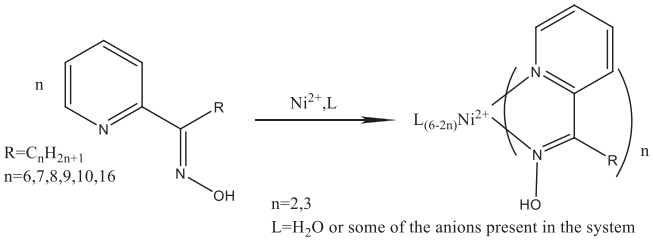
31a



R=CH_3, *n*-$C_{12}H_{25}$

31b

Hampl et al. [83e] studied coordination of lipophilic alkyl pyridin-2-yl ketoximes **32** to Ni^{2+} ions, reduction of lipophilic 3-alkoxyacetophenones with sodium borohydride, and alkaline hydrolysis of NPDPP as probes to investigate the factors influencing reactivity of organic compounds in micellar systems. From the results of kinetic investigations it was concluded that the contribution of coulombic forces between the micellar surface and the reagent approaching the aggregate and increased local concentration of the reactions are sometimes overestimated.



32

They suggested that the observed reactivity in micelles can be strongly influenced by various other factors.

12. Conclusions

Oximate ions in self-assembled systems act as catalytic nanoreactors providing a convenient approach to combat OPCs toxicity. Also, such formulation increases oxime reactivity, solubilizes highly lipophilic substrates (nerve agents and pesticides) and enhances the degradation reactions of the toxic esters and nerve agents. Promising results have been obtained with oxime functionalized nano-aggregates over simple oximate ions in the micellar solutions. The present review summarizes some remarkable contributions in this context. Despite the existence of numerous reports on detoxification chemistry, a promising favorable decontamination system against OPC toxicity is still lacking and the future scope lies in more extensive investigations in various media including microemulsions and vesicles. The present report emphasizes the promising role of oximate ion as functional nanoreactors which need to be deeply explored and optimized in the near future.

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