Technologies for elimination of chemical hazards

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Modern approaches to the development of efficient organized microheterogeneous surfactant-based systems for decomposition of organophosphorus compounds – a review

Tatiana M. Prokop'eva[1], Alla B. Mirgorodskaya[2], Irina A. Belousova[1], Tatiana M. Zubareva[1], Maria K. Turovskaya[1], Boris V. Panchenko[1], Nina G. Razumova[1], Tatiana S. Gaidash[1], and Vasiliy A. Mikhailov[1]✉

[1]Public Institution "L.M. Litvinenko Institute of Physical Organic and Coal Chemistry", Donetsk, Ukraine, e-mail: v_mikhailov@yahoo.com
[2]A.E. Arbuzov Institute of Organic and Physical Chemistry, FRC KazSC of RAS, Kazan, Russia

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Abstract – Ascertaining regularities in the effects of organized media on reactivity of organic compounds, establishing of quantitative relationships «structure – property – micellar effects», and searching for efficient ways of structure modifications and functionalization of microorganized systems offer broad potentials for governing the reaction rates. A good choice for decomposition of ecotoxic substrates is the use of reaction media agreeable to "green chemistry" criteria. Solutions of surfactants can serve these purposes. Three approaches were used in designing highly efficient organized microheterogeneous systems (OMS) suitable for development of catalytic systems on the basis of dimeric surfactants. The first involves structure variations in cationic surfactants for alkaline hydrolysis (length of spacer and tail, the nature of head group, and so on). The second consists in design of surfactants with reactive counterion; dihalogenohalogenates are the sources of nucleophilic-oxidizing species with a broad spectrum of activity. The third approach involves design of functionalized surfactants which are several orders of magnitude more efficient than their non-functionalized counterparts. Micellar effects in decomposition of 4-nitrophenyl esters of diethylphosphonic, diethylphosphoric and toluenesulfonic acids reach ~ 10^2 in alkaline hydrolysis, and 10^4 in the systems involving functionalized surfactants. The reagent concentrating and change in nucleophilic reactivity by transferring the reaction from water into the micellar pseudophase contribute significantly to the observed rate acceleration. Hydrophobic properties of surfactant and substrate, mainly the nature of the head group and spacer-are essential.

Keywords: organophosphorus compounds, cationic and dicationic surfactants, micellar catalysis

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Технологии ликвидации источников химической опасности

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Современные подходы к разработке эффективных организованных микрогетерогенных систем на основе детергентов для разложения фосфорорганических соединений. Обзор

Т. М. Прокопьева[1], А. Б. Миргородская[2], И. А. Белоусова[1], Т. М. Зубарева[1], М. К. Туровская[1], Б. В. Панченко[1], Н. Г. Разумова[1], Т. С. Гайдаш[1], В. А. Михайлов[1]✉

[1]Государственное учреждение «Институт физико-органической химии и углехимии им. Л.М. Литвиненко», Донецк, Украина, e-mail: v_mikhailov@yahoo.com
[2]Институт органической и физической химии им. А.Е. Арбузова, ФИЦ КазНЦ РАН, Казань, Россия

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Аннотация – Выяснение закономерностей влияния организованных сред на реакционную способность органических соединений, установление количественных закономерностей «структура–свойство–мицеллярные эффекты» и поиск путей модификации и функционализации микроорганизованных систем открывают широкие перспективы управления скоростями химических реакций. Решение такой задачи напрямую связано с минимизацией актов террористического воздействия и техногенных аварий. Разложение субстратов-экотоксикантов предполагает использование реакционной среды, удовлетворяющей критериям «Green chemistry», что является необходимым условием, и таковыми выступают растворы ПАВ. Для создания высокоэффективных организованных микрогетерогенных систем (ОМС) для катализа на основе димерных ПАВ были реализованы три следующих направления. Первое – варьирование структуры катионных ПАВ в реакциях щелочного гидролиза. Второе – конструирование ПАВ с реакционноспособным противоионом (дигалогенгалогенат) – системы широкого спектра действия, одновременно выступающей источником нуклеофильно-окислительного реагента и реализующей преимущества ОМС. Третье – формирование функционализированных наноразмерных ансамблей, обладающих на порядки более высокой эффективностью, чем не функционализированные. Мицеллярные эффекты в реакциях разложения 4-нитрофениловых эфиров диэтилфосфоновой, диэтилфосфорной и толуолсульфоновой кислот достигают ~ 10^2 (щелочной гидролиз) – 10^4 раз (системы на основе функционализированных ПАВ). При этом основной вклад в наблюдаемое ускорение при переносе процесса из воды в мицеллярную псевдофазу вносят эффекты концентрирования реагентов и изменение нуклеофильной реакционной способности. В этом случае важное значение имеют гидрофобные свойства ПАВ и субстратов, природа катионной части головной группы и мостикового звена.

Ключевые слова: фосфорорганические соединения, катионные и дикатионные ПАВ, мицеллярный катализ.

INTRODUCTION

Decomposition of ecotoxicants (pesticides, chemical warfare agents, including highly toxic organophosphorus compounds (OPC) [1]) poses an acute problem which is directly connected with environmental safety, minimization of consequences of technogenic accidents and terrorist attacks. All of these require comprehensive studies involving examination of the reactivity of currently available systems for decomposition of ecotoxicants, an evaluation of the factors governing the rates of their destruction, and development of the theoretical basis for quantitative assessment of “structure-property-reactivity” relationships in such systems [2–10].

Recent works in the field show considerable promise from both of “normal” and α-nucleophiles for organized microheterogeneous systems (micellar solutions,

microemulsions, etc.). This way we can provide a means for development of the systems characterized by high efficiency, versatility, simplicity and safety in operation [2–12].

An alkaline hydrolysis is one of the simplest reactions used in decomposition of organophosphorus compounds in water [13–18]. Reaction rates of phosphorus acid esters are not very large, and require concentrated alkaline solutions to use, which are extremely aggressive media. Highly reactive inorganic α-nucleophiles, HOO^- and ClO^- anions are of particular interest as basic constituents of formulations for decomposition of ecotoxicants. For obvious reasons, detailed studies of reaction mechanisms involving α-nucleophiles, and development of the formulations on their basis were carried out with chemical warfare agents [18–24]. Nucleophilic attack of peroxide anion on phosphorus atom results in a fast decomposition of OPC to form peroxy acids followed by their hydrolysis. Predominant research activity in the last years was focused on the development of universal systems on the basis of hydrogen peroxide. In such systems HOO^- ion and H_2O_2 serve as a nucleophilic and oxidizing agent, respectively. However, H_2O_2 is a weak oxidizer, and hence the advanced methods of its activation with the use of peroxycarbonates, peroxymolibdates, and others were proposed [25, 26]. In this respect the systems involving hypochlorous acid derivatives exhibit a wide spectrum of action. Despite the pronounced nucleophilic-oxidizing properties of $HClO/ClO^-$ couple, hypochlorite solutions have a number of essential disadvantages such as low storageability, high corrosiveness, toxicity, etc.

A further group of highly reactive α-nucleophiles, namely, hydroxylamine derivatives – oximes, amidoximes and hydroxamic acids, – is worthy of note. All of these are capable of "mild" decomposition of OPC and can serve as efficient antidotes - reactivators of OPC-inhibited acetylcholinesterase [27–34].

It is unlikely that further increase in reactivity of α-nucleophiles can be obtained by their structural modification. An examination of Brønsted relationships for anionic oxygen α-nucleophiles revealed that hydroxylamine anion (pK_a 13.71) reaches the maximum possible reactivity (Fig. 1) [35–36]. Hence, design of suitable nucleophilic-oxidizing reagents requires new approaches, namely, further search for activators of H_2O_2, preparation of the stable solid sources of "active" halogen, and, finally, wide structure variations of hydroxylamine derivatives, first of all, low-basicity oximes, for efficient detoxification under mild conditions.

As was mentioned above, one of the ways for preparation of efficient reagents is the use of organized microheterogeneous systems (OMS) - micelles, lamellar structures, microemulsions. Such systems have an obvious merit, that is, compatibility with the requirements of "green chemistry". Recently a special attention is given to decomposition of OPC in the presence of surfactants. Firstly, micellar solutions provide ~10^2 – 10^3 fold increase in the reaction rates as compared with those in water. Secondly, variations in experimental conditions make it possible to control the reaction rates.

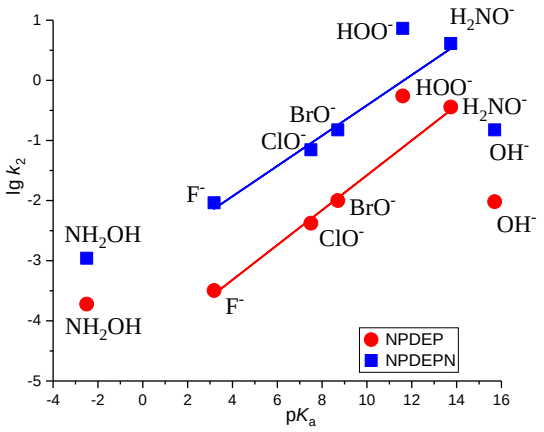


Fig.1. Brønsted plots for reaction of 4-nitrophenyl diethylphosphate (NPDEP) and 4-nitrophenyl diethylphosphonate (NPDEPN) with inorganic α-nucleophiles; μ 1.0 M (KCl), 25°C.

Thirdly, the use of OMS facilitates the solubilization of OPC which are only slightly soluble in water. And, finally, an increase in reaction rates due to micellar catalysis is observed at extremely low, down to $10^{-3}-10^{-2}$ M, concentration of surfactant. Additionally, modifications in the surfactants can give rise to biodegradable compounds [37–41].

Transferring the reaction from water into micellar pseudophase, an increase in observed reaction rates ($k_{obs.}$, s^{-1}) is caused mainly by reagent concentrating in micelles [13–16, 28–30, 37, 42–46]. In this case a change in nucleophilic reactivity is not too large, whereas the second-order rate constant ($k_2^{m.}$, $M^{-1}s^{-1}$) can both increase and decrease relative to those in water (k_2^{w}, $M^{-1}s^{-1}$) [14–16, 28–30, 42].

Below are given three approaches employed in designing the organized catalytic systems on the basis of monomeric and dimeric surfactants.

The first approach consists in structure variations of cationic surfactants in alkaline hydrolysis of OPC. Wide diversity in the structure variations of the cationic moiety in the head group, spacer and alkyl "tail", together with the "surfactant structure – property – micellar effects" relationships can provide a basis for the development of formulations, compositionally simple and economically more attractive for removal/detoxication of OPC.

The second involves the use of new sources of "active" halogen which exhibit a wide range of action. Such surfactants with a reactive counterion are unique in that they can act as the sources of both nucleophilic and/or oxidizing agent.

And, finally, the third approach lies in development of functionalized assemblies, which, as the natural enzyme compounds, are by orders of magnitude more efficient than their non-functionalized counterparts.

To resolve the problems in these directions, detailed studies required on micelles formation (and, more generally, aggregation) in aqueous solutions and other organized media, coupled with ascertaining the driving forces of such processes. Dicationic surfactants are capable of forming supermolecular assemblies whose structure is outside the scope of long-held views on micelle formation [42]. Studies on the behavior of such assemblies and design of new sources of "active" halogen

necessitate the use of modern experimental techniques developed in the past decade [42–43].

In some respects, the present study is a generalization of our findings; also included are some considerations regarding the future research. Hence the present brief review does not include comprehensive evaluation of a body of information available in literature on this problem. The most relevant publications will be cited in the subsequent discussion as needed. To be more specific, we attempted to give a number of the most representative examples of our findings on decomposition of ecotoxic compounds in micellar solutions and discuss some approaches useful in designing new surfactants which make it possible to govern the rates and courses of micellar reactions under mild conditions (pH, temperature, concentration).

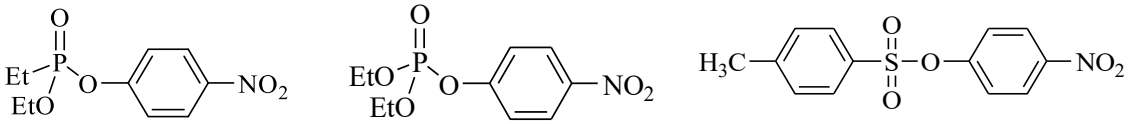
EXPERIMENTAL SECTION

Synthesis and purification of the substrates, 4-nitrophenyl esters of diethyl phosphonic, diethyl phosphoric and toluenesulfonic acids, was described elsewhere [44, 45]. Ethanediyl-1-2-bis(dimethylalkylammonium) and propanediyl-1,2-bis(dimethylhexylammonium) dibromides were synthesized as reported in [46–48]. Synthesis and purification of dimeric surfactants with the spacers containing hydroxy and ester moieties were described in [46, 48]. Preparation of dibromobromates with a varied cationic fragment and dibromobromates of dicationic surfactants was described elsewhere [49-51]. Functionalized surfactants were synthesized similarly to the procedures described in [44, 45, 52–55]. Structure and purity of the compounds was confirmed by elemental analysis and ^{1}H NMR techniques. ^{1}H NMR spectra were recorded on a Bruker NMR spectrometer Avance-II-400 (400 MHz for protons).

RESULTS AND DISCUSSION

Substrates

Hydrolysis of 4-nitrophenyl esters of dietylphosphonic (NPDEPN), diethylphosphoric (NPDEP) and toluenesulphonic (NPOTos) acids (Fig. 2) was picked as model process for decomposition of widely used ecotoxicants.



NPDEPN NPDEP NPOTos

Fig. 2. Structure of substrates.

The substrates were selected relying on the following considerations. The first two substrates are organophosphorus compounds, one of them, NPDEP, was widely used as a pesticide [1]. The esters of phosphoric and phosphonic acids are similar in their hydrophobic properties, whereas the reactivity of NPDEPN is ten times that of NPDEP. At the same time, k_2^w (NPOTos) ≈ k_2^w (NPDEP), $M^{-1}s^{-1}$ [31–33, 35, 36], whereas the solubilizing efficiency of tosylate is an order of magnitude higher than that of organophosphorus compounds [44]. It makes possible with this set of

substrates to trace the impact of the reaction center electrophilicity and substrate hydrophobic properties on micellar effects.

Alkaline hydrolysis of substrates

During the last two decades new possibilities in designing the organized microheterogeneous systems were associated with dimeric (Gemini) surfactants [2, 4–6, 32, 36, 41–43, 64–70]. Structure variations in spacer and head groups can give rise to a wide diversity of dimeric surfactants, including the compounds with enhanced affinity for water due to the presence of hydroxyl groups, as well as ether and carbonyl oxygen atoms. It is this structure feature was proved to be responsible for physico-chemical specificity of dimeric surfactants. Recent studies showed that the aqueous microheterogeneous systems with extremely low concentration (down to 10^{-3} M) of dimeric surfactants are highly favorable reaction media for hydrolytic decomposition of the esters of carboxylic [16] and phosphoric [71, 72] acids.

Kinetic regularities in decomposition of substrates by hydroxide ion

Kinetic behavior of surfactants I–IV, VI and VII in decomposition of NPDEPN, NPDEP and NPOTos by hydroxide ion has been studied in details [13, 16, 37, 51]. Micellar effects of the dimeric surfactants were compared with those of cetyltrimethylammonium bromide (CTAB, V).

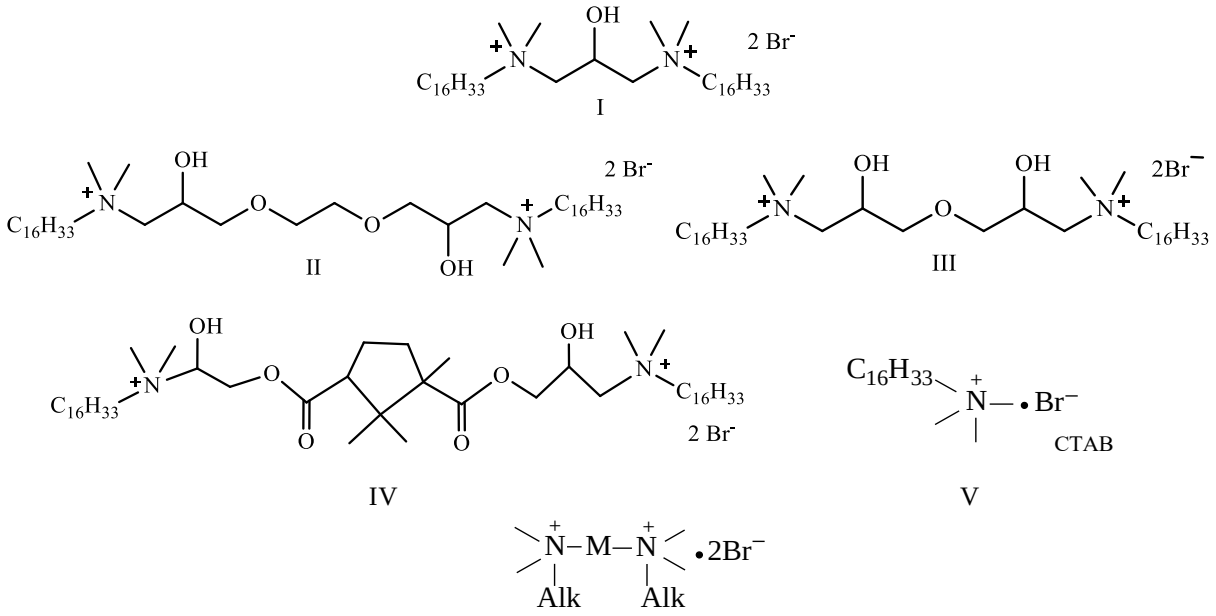


Fig. 3. Structure of dimeric cationic (I–IV) and tetraalkylammonium (VI, VII) surfactants, and CTAB (V).

An introduction of hydroxyl groups into the spacer fragment of the dimeric surfactants can give rise to micellar catalytic systems with low Krafft temperature and highly polar microenvironment, which is favorable to the closest approach of small hydrophilic ions and hydrophobic substrates in the micellar pseudophase. Fig. 4 (a, b) gives the plots «$k_{obs.}$– pH» at a constant c_0, and «$k_{obs.} – c_0$ » at a constant pH for decomposition of NPDEPN in the presence of dimeric surfactants and monomeric

CTAB (V). The observed rate constants increase both with pH and surfactant concentration; a maximum micellar catalytic effect is no more than ~ 10^2-fold (Table 1).

Experimentally, alkaline hydrolysis proceeds through two parallel routes in micellar (m) and aqueous (w) phases with the second-order rate constants, k_2^w and k_2^m ($M^{-1}\cdot s^{-1}$) for hydroxide ion in water and micelles, respectively (Scheme 1).

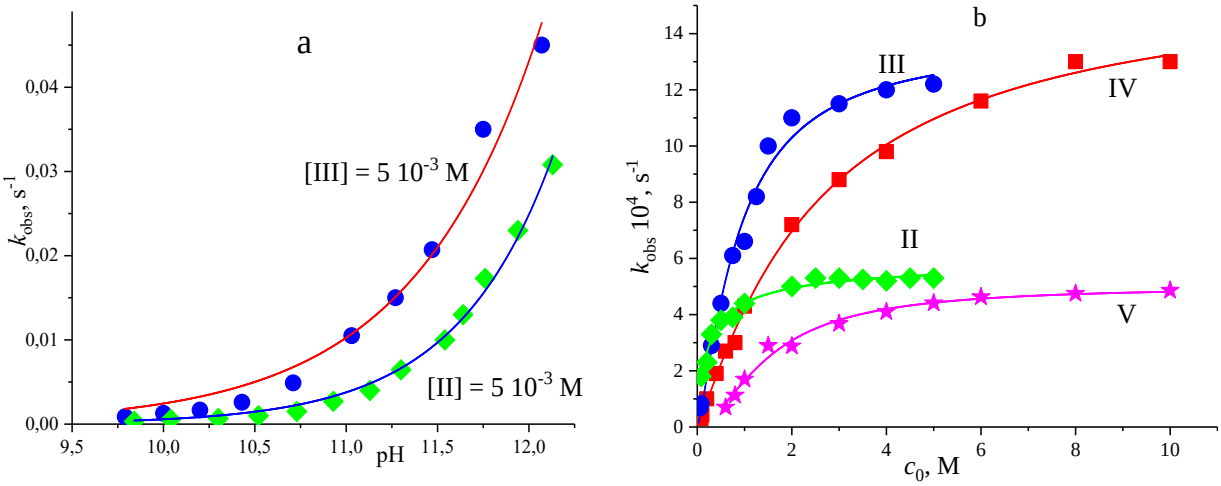


Fig. 4. Observed rate constants ($k_{obs.}$, s^{-1}) vs pH (a) and concentration of surfactant (c_0, M), pH 10.0 (b) in reaction of NPDEPN with hydroxide ion; 25°C

Table 1. Observed rate constants of alkaline hydrolysis of NPDEPN in water and in the presence of dimeric surfactants; micellar catalytic effects

Surfactant	pH 10.0, c_0 $2\cdot10^{-3}$ M			pH 10.0, c_0 $5\cdot10^{-3}$ M		
	$k_{obs.}$, s^{-1}	$k^m_{obs.}/k^w_{obs.}$	$k^m_{obs.}/k^{CTAB}_{obs.}$	$k_{obs.}$, s^{-1}	$k^m_{obs.}/k^w_{obs.}$	$k^m_{obs.}/k^{CTAB}_{obs.}$
I	$7.10\cdot10^{-4}$	47	2.5	-	-	-
II	$5.30\cdot10^{-4}$	35	1.8	$5.30\cdot10^{-4}$	36	1.2
III	$1.15\cdot10^{-3}$	77	4	$1.22\cdot10^{-3}$	81	2.8
IV	$7.20\cdot10^{-4}$	48	2.9	-	-	-
V	$2.88\cdot10^{-4}$	19	-	$4.41\cdot10^{-4}$	29	-
water	$1.50\cdot10^{-5}$	-	-	$1.50\cdot10^{-5}$		-

$$\begin{array}{ccccc} (S)_w & + & (HO^-)_w & \xrightarrow{k_2^w} & \\ \downarrow\uparrow P_S & & \downarrow\uparrow P_{HO^-} & & \text{Products} \\ (S)_m & + & (HO^-)_m & \xrightarrow{k_2^m} & \end{array} \qquad (1)$$

Partitioning of the substrate and reagent between aqueous and micellar pseudophase is defined by the corresponding partition coefficients:

$$P_S = [S]_m / [S]_w \qquad (2)$$

$$P_{HO^-} = [HO^-]_m / [HO^-]_w$$

Kinetic data were treated using pseudophase partitioning model (PPM) [63, 65, 72, 74]. Taking into account the Scheme 1 and equation 2, the observed reaction rate ($k_{obs.}$, s^{-1}) is well represented by the expression

$$k_{obs.} = \frac{(k_2^m/V_m)K_S \cdot K_{HO^-} \cdot c + k_2^w}{(1+K_S c)(1+K_{HO^-} c)} \cdot [HO^-]_0 = \frac{k_m \cdot K_S \cdot K_{HO^-} \cdot c + k_2^w}{(1+K_S c)(1+K_{HO^-} c)} \cdot [HO^-]_0 , \quad (3)$$

where $c = c_0 -$ cmc, M; cmc is the critical micelle concentration [75–78]; c_0 is the analytical concentration of the surfactant; V_m, M^{-1} is the partial molar volume of the surfactant [75, 79]; $K_S \approx P_S \cdot V_m$ and $K_{HO^-} \approx P_{HO^-} \cdot V_m$, M^{-1} are the binding constants for substrate and nucleophile, respectively; k_2^w and k_2^m, $M^{-1}s^{-1}$ are the second-order rate constants for HO^--ion reaction in aqueous and micellar pseudophase; $k_m = (k_2^m/V_m)$, s^{-1} is the reduced rate constant of reaction in micellar pseudophase.

Equation (3) describes experimental results well over the whole concentration range.

An environmentally friendly system on the basis of dimeric surfactant IV involving ester groups is of special practical interest. Hydrolysis of the ester bond in the surfactants proceeds under the conditions different from those in decomposition of OPC. After completion of the reaction, further conversions can be achieved by changing pH in the system [37].

Table 2 gives physicochemical characteristics and micellar effects in surfactant IV catalyzed alkaline hydrolysis of organophosphorus esters.

Table 2. Micellar catalytic effects in OMS based on surfactant IV in alkaline hydrolysis of esters

Substrate	pH	k_2^m, $M^{-1}\cdot s^{-1}$*	K_S, M^{-1}*	k_2^w, $M^{-1}\cdot s^{-1}$**	k_2^m / k_2^w	$k_{obs.}^m / k_{obs.}^w$ ***
NPDEPN	10.7	0.13	100	0.15	1.2	64
NPDEP	11.0	0.13	100	0.01	13	870
NPOTos	10.5 11.0 11.5	0.006 0.013 0.017	2200 1950 1400	0.01	0.6 1.3 1.7	3000

*Calculated from equation (3).

**From [35].

***Observed rate constants $k_{obs.}^m$ at c_0 0.01 M.

Kinetics data for surfactants VI and VII were treated similarly to those for surfactants I–IV in a frame of PPM, only the distribution of substrate was accounted (Scheme 4, equation 5):

$$D_n + [S]_w \underset{}{\overset{K_S \cdot}{\rightleftharpoons}} [S]_m \quad (4)$$

$[S]_w \rightarrow$ Products (k_2^w); $[S]_m \rightarrow$ Products (k_2^m)

$$k_{obs.} = \frac{\chi \cdot k_m K_S c + k_2^w [HO^-]}{1 + K_S c}, \quad (5)$$

where χ is the mole fraction of dimeric surfactant. Decomposition of substrates was studied both in comicellar systems and solutions involving only cationic (or functionalized) surfactants. An increase in the length of alkyl substituent results in decreased water solubility of surfactants, and maximum reachable range of concentrations may be not enough for good quality constants evaluation. It is this circumstance which necessitates the use of comicelles.

Factors responsible for micellar effects

Micellar effects in alkaline hydrolysis can be described in terms of $k^{m}_{obs.}/k^{w}_{obs.}$ ratios under the same experimental conditions (pH, c_0, and temperature). In the presence of surfactants, $k^{m}_{obs.}/k^{w}_{obs.}$ ratios reach the values up to 10–10^3 (Tables 1–3). In this case the nature both of surfactant and substrate is essential. In alkaline hydrolysis of the esters studied the main factors responsible for increased observed reaction rates in the presence of surfactants are the effects of reagent concentrating and changes in microenvironment. Micellar effects in surfactants I–IV exceed those in their monomeric counterpart, CTAB, (Fig. 4, b) whereas in surfactants VI and VII the corresponding values increase with the length of alkyl "tail" (Fig. 5, Table 3).

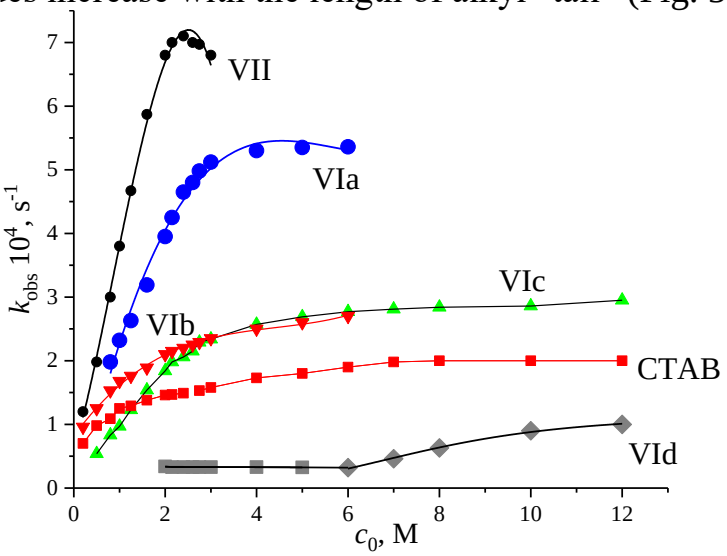


Fig.5. Observed rate constants ($k_{obs.}$, s^{-1}) vs concentration of surfactant (c_0, M) in reaction of NPDEPN with hydroxide ion in micelles; pH 10.0, 25°C.

Effects of reagent concentrating are, above all, representative of the ability of micellar pseudophase to solubilize a variety of compounds [65]. In aqueous micelles the solubilization depends on the hydrophobicity and biphilicity of solubilizate. NPDEPN, NPDEP and NPOTos are electrically neutral species and for the most part their binding with the micelles is determined by hydrophobic interactions. Efficiency of substrate solubilization can be described in terms of the binding constants K_S. The values of K_S for NPDEPN, NPDEP and NPOTos in micellar pseudophase of I–III were found to be ~ 300, 250 and 3000 [44], whereas in the micelles of IV under the same experimental conditions the binding constants are somewhat lower (Table 2). Such behavior of K_S may be caused by a number of factors. Firstly, «loose», water-saturated micellar surface of IV can decrease solubilizing power of the micelle toward hydrophobic substrates. On the other hand, such structure of micelle can favor the closest approaching of small hydrophilic ions and solubilized ethers, thus giving

rise to high values of the observed effect. Secondly, compound IV is readily soluble in water up to the concentrations by two orders of magnitude higher than cmc. As is known [65], most of cationic dimeric surfactants form aggregates of higher orders at fairly low concentrations. It is not unlikely that an increase in concentration of surfactant IV is accompanied by morphological rearrangement of aggregates, in which case the binding constants and V_m should be used with caution. The same order of changes in K_S was observed for OMS involving not only dimeric but their parent monomeric surfactants as well [54, 57, 61, 62].

Table 3. Physico-chemical characteristics of alkaline hydrolysis of NPDEPN in the presence of surfactants VI, VII, CTAB and comicelles VI/CTAB and VII/CTAB

Substrate	χ*	k_m, s^{-1}**	$k_2^m \cdot 10^4$, $M^{-1} \cdot s^{-1}$***	K_S, M^{-1}****	$k_{obs.}^m / k_{obs.}^w$ *****
16-3-16 (VII)	1,0	$2,6 \cdot 10^{-3}$	15	171	170
16-2-16 (VIa)	1,0	$2,6 \cdot 10^{-3}$	15	107	170
	0,5	$1,2 \cdot 10^{-3}$	7,2	190	80
	0,25	$7,42 \cdot 10^{-4}$	4,43	202	50
	0,1	$4,68 \cdot 10^{-4}$	2,79	235	31
14-2-14 (VIb)	1,0	$4,74 \cdot 10^{-4}$	2,83	443	32
12-2-12 (VIc)	1,0	$5,00 \cdot 10^{-4}$	2,98	256	33
	0,5	$3,60 \cdot 10^{-4}$	2,15	472	24
	0,25	$5,22 \cdot 10^{-4}$	3,12	345	35
	0,1	$5,28 \cdot 10^{-4}$	31,5	473	35
10-2-10 (VId)	1,0	$1,19 \cdot 10^{-4}$	0,71	420	8
	0,5	$3,31 \cdot 10^{-4}$	1,98	483	22
	0,25	$4,74 \cdot 10^{-4}$	2,83	422	49
	0,1	$5,60 \cdot 10^{-4}$	3,34	357	37
CTAB	1,0	$3,42 \cdot 10^{-4}$	2,04	584	23

*Mole fraction of dimeric surfactant in comicelles with CTAB.
**Reduced first-order rate constant.
***Reactivity of hydroxide ion in micellar pseudophase.
****Binding constant of substrate.
*****Micellar effect of surfactant at pH 10,0 and 25°C.

Effects of reagent concentrating are, above all, representative of the ability of micellar pseudophase to solubilize a variety of compounds [65]. In aqueous micelles the solubilization depends on the hydrophobicity and biphilicity of solubilizate. NPDEPN, NPDEP and NPOTos are electrically neutral species and for the most part their binding with the micelles is determined by hydrophobic interactions. Efficiency of substrate solubilization can be described in terms of the binding constants K_S. The values of K_S for NPDEPN, NPDEP and NPOTos in micellar pseudophase of I–III were found to be ~ 300, 250 and 3000 [44], whereas in the micelles of IV under the

same experimental conditions the binding constants are somewhat lower (Table 2). Such behavior of K_S may be caused by a number of factors. Firstly, «loose», water-saturated micellar surface of IV can decrease solubilizing power of the micelle toward hydrophobic substrates. On the other hand, such structure of micelle can favor the closest approaching of small hydrophilic ions and solubilized ethers, thus giving rise to high values of the observed effect. Secondly, compound IV is readily soluble in water up to the concentrations by two orders of magnitude higher than cmc. As is known [65], most of cationic dimeric surfactants form aggregates of higher orders at fairly low concentrations. It is not unlikely that an increase in concentration of surfactant IV is accompanied by morphological rearrangement of aggregates, in which case the binding constants and V_m should be used with caution. The same order of changes in K_S was observed for OMS involving not only dimeric but their parent monomeric surfactants as well [54, 57, 61, 62].

Binding constant K_S, as a measure of solubilization efficiency of substrate, increases with decreased length of the alkyl chain in surfactants VI and VII (Table 3). Such a behavior is somewhat surprising. By contrast, a distinctly different interrelation between the binding constants and length of alkyl "tail" was observed in dimeric cationic and functionalized imidazolium surfactants: both K_S and micellar effects increase with the number of methylene units [62, 63, 71]. Here, the effects of reagent concentrating are of crucial importance in the micellar "catalysis". Unconventional change in efficiency of substrate solubilization in the micelles of tetraalkylammonium surfactants was also found for functionalized surfactants as well [71]. It should be emphasized that the ease of structure modification – quasi-spherical, rod- and thread-like, etc. - is characteristic for dimeric surfactants including those with cationic fragment $-N^+Alk_3$ in their head group [72]. To minimize the contact of spacer with water molecules, micellar aggregates of dimeric surfactants 16-n-16 at $n \leq 3$ (VIa, VII) take the form of worm-like threads. Micelles of this type supposedly provide more favorable conditions than those of CTAB. Nevertheless, thread-like micelles with n = 4 were found to have an optimum spacer length in order to provide the highest reactivity [72].

Micellar microenvironment is a further important factor affecting the rates of alkaline hydrolysis. Tables 1-3 give the second-order reaction rates $k_2^m = k_m \cdot V_m$ as a measure of nucleophilicity of hydroxide ions. As evidenced by the data in Table 2, changes of reactivity in the micellar pseudophase IV is unlike those in water: k_2^m(NPDEPN) ≈ k_2^m(NPDEP) ≈10 k_2^m(NPOTos) and k_2^w(NPDEPN) ≈ 10 k_2^w(NPDEP or NPOTos). Micelles of functionalized surfactants normally exhibit maximum k_2^m for phosphonate ester as opposed to that in the presence of IV. It is not clear why nucleophilicities of hydroxide ion toward phosphonate and phosphate esters in micellar pseudophase (k_2^m) are similar. It is unlikely that the sharp structure changes in the transition state are responsible for the observed effect. In essence, micellar effects in surfactant IV correlate with the changes in binding constants of substrates and nucleophilicity of hydroxide anions in alkaline hydrolysis. They have highest values for NPOTos and decrease in passing to phosphonate and phosphate esters (Fig. 6).

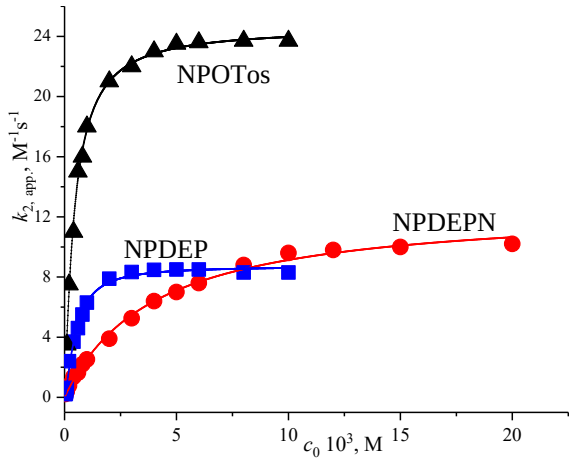


Fig.6. Apparent rate constants ($k_{2,app.}$, $M^{-1}s^{-1}$) vs concentration of surfactant IV (c_0, M) in alkaline hydrolysis of NPDEPN, NPDEP and NPOTos; borate buffer, pH 11.0, 25°C.

The second-order rate constants in the micellar pseudophase, k_2^m, for surfactants VI and VII are significantly lower than that in aqueous phase (k_2^w = 0.15 $M^{-1}s^{-1}$) [35] (Table 3). This is very usual for cationic surfactants catalyzed alkaline hydrolysis [46–48, 63, 67, 71–74]. Nonetheless, as already mentioned above, the micellar effects result in ~ 10–10^2-fold acceleration. Such a situation is not uncommon. Provided that the reagents are concentrated in a small volume of the micelle, the overall reaction rates will be increased even though the second-order rate constants in micelles are lower than those in water. The observed changes in micellar effects are primarily due to favorable partitioning of the substrate between water and micellar pseudophase. Noteworthy also that an increase in the observed rate constants of alkaline hydrolysis in micelles of surfactant IV is predominantly caused by the effects of reagent concentrating, except for interaction of hydroxide ion with NPDEP. Indeed, a comparison of k_2^m/k_2^w and $k_{obs.}^m/k_{obs.}^w$ from Table 2 suggests that the reagent concentration is not the only factor responsible for an increase in reaction rates.

For practical purposes the regularities of physicochemical properties (cmc, K_S) changes provide a basis for selection of strategies for targeted structure modification of surfactants to obtain the supernucleophilic OMS suitable for decomposition of OPC. Thus, a decrease in the length of alkyl substituent results in enhanced water solubility of surfactants thus suggesting their advantage over long-chain ones. Alternatively, the water solubility of the sparingly soluble surfactants may be partially increased by the use of comicellar systems involving CTAB or their parent monomeric surfactant. Moreover, the mixtures of structurally different micelles in different ratios act as aggregates whose properties (on average) resemble those of their constituents [80]. Effects of CTAB in comicelles VIa/CTAB and VIc/CTAB are entirely different: in the former case $k_{obs.}$(VIa/CTAB) → $k_{obs.}$(VIa), whereas in the latter case $k_{obs.}$(VIc/CTAB) → $k_{obs.}$ (CTAB).

As a final remark, it should be noted the following. Dimeric surfactants I–IV, VI and VII involving long-chain alkyl “tail” exhibit abnormally low cmc, and, hence, similar accelerations of alkaline hydrolysis can be reached at concentrations of surfactant by an order of magnitude lower than those for CTAB (for instance,

$k_{obs} \approx 7.5\ 10^{-4}\ s^{-1}$ for NPDEPN decomposition in OMS based on CTAB can attain at $c_0 = 0.02$ M; in OMS based on V at $c_0 = 0.0021$ M). In addition, the micellar effects are undoubtedly affected by aggregate morphology which is directly dependent on the spacer structure. Hence, variation in the spacer structure is a possible way of modifying the dimeric surfactants to obtain supernucleophilic systems on the basis of "normal" nucleophile – hydroxide ion.

New sources of "active" halogen as a basis for nucleophilic-oxidizing systems

Inorganic α-nucleophiles exhibit abnormally high reactivity in acyl transfer reactions, much superior (10^2–10^5 times) to that of their "normal" counterparts of commensurable basicity. Hypobromite anion, BrO^-, is a representative of such compounds. Its conjugated acid, HOBr, is a powerful oxidizer, so the system $HOBr/BrO^-$ can be used as a nucleophilic-oxidizing couple to provide both nucleophilic decomposition of acyl substrates (ecotoxicants included) and higher degree of destruction of the reaction products [81–82].

Bis(dialkylamide)hydrogen dihalogenates as efficient agents for decomposition of OPC in water. Considerable attention has been paid recently to the studies of solid-phase carriers of bromine and new fields of their use in chemical transformations – bromination, co-halogenation, oxidation, cyclization, ring opening, substitution and hydrolysis. Quaternary ammonium tribromides find application in organic synthesis [83–89]. Bis(dialkylamide)hydrogen dihalogenates (VIII–XI) integrate high "active" bromine content, prolonged storage life (more than ten years for VIII) and water solubility [82, 89].

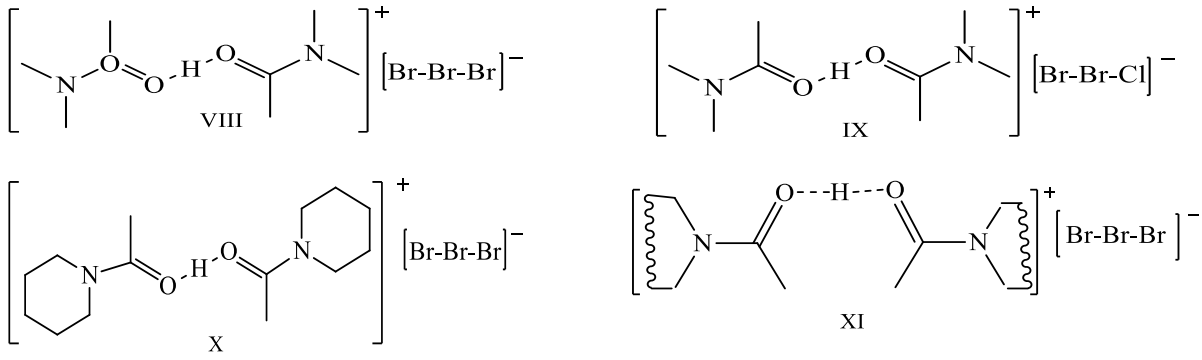
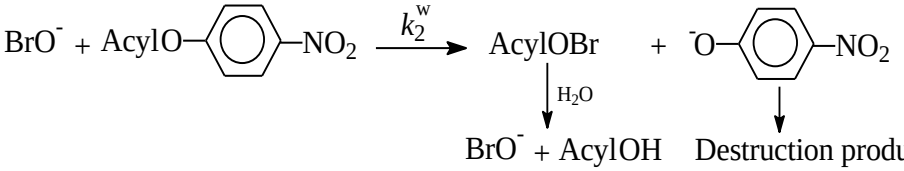


Fig. 7. Structure of dihalogenates VIII–XI.

Dissolved in water, dibromobromates yield dibromobromate anion followed by fast and reversible dissociation to form bromide anion and bromine, which then, depending on the acidity of medium, yields HOBr, BrO^- or $HOBr/BrO^-$. Attack of BrO^--ion on electron-deficient center of substrate results in formation of 4-nitrophenolate ion as a reaction product which undergo destruction with the participation of HOBr (or $HOBr/BrO^-$):



(6)

Nucleophilic reactivity of hypobromite anion generated from the various sources of active bromine was studied under conditions for which the contribution from the reaction path responsible for oxidation of 4-nitrophenolate ion is negligibly small: no loss in 4-nitrophenolate anion was observed during 5 - 10 half-lives of the reaction. Reactions were carried out at specified pH with due regard for the ratios of rate constant of nucleophilic attack on the electron-deficient center of substrate to that of oxidation of 4-nitrophenolate anion. The value of pH for NPDEPN was 11.15, and those for NPDEP and NPOTos were more than 11.35. Fig. 8 shows typical time variations in absorbance of 4-nitrophenolate ion during the reaction of hypobromite ion from bis(N,N-dimethylacetamide)hydrogen dibromobromate with NPDEPN at various pH, and those in decomposition of 4-nitrophenol. The ascending curves illustrate an accumulation of 4-nitrophenolate ion in the system, and descending curve describes 4-nitrophenolate destruction. Under these conditions the observed rate constant $k_{obs.}$, s^{-1} is described by equation:

$$k_{obs.} = k^{w}_{2,OH}[HO]^{-} + k^{w}_{2,BrO^{-}}[HOBr]_{o}\alpha_{BrO^{-}}, \qquad (7)$$

where $k_2^w[HO]^-$, s^{-1} is the contribution from alkaline hydrolysis; $[HOBr]_0$, M is the analytical concentration of hypobromous acid; α_{BrO^-} is the fraction of BrO^- anion; and k^{w}_{2,BrO^-}, $M^{-1}s^{-1}$ is the second-order rate constant, describing the nucleophilicity of hypobromite anion in water.

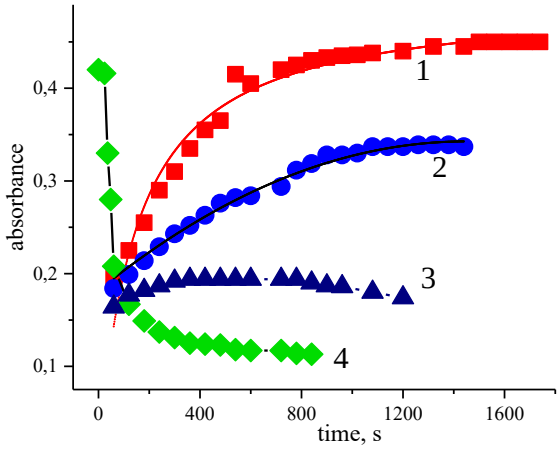


Fig.8. Time dependence of absorbance in reaction of HOBr/BrO^- from bis(N,N-dimethylacetamide) hydrogen dibromobromate (VIII) with NPDEPN and 4-nitrophenolate anion; $[HOBr]_o$ = 0.01 M; pH 11.15 (1), 10.6 (2), 10.5 (3), and $[HOBr]_0$ = 0.005 M, pH 9.6 (4); λ 420 nm, water, 1 M KCl, 25°C.

Since the acid ionization constant pK_a of hypobromous acid is taken to be 8.69 and $\alpha_{BrO^-} \rightarrow 1$ (pH 11.15, α 0.996; pH 11.35, α 0.998), equation (7) can be written as

$$k_{obs.} = k^{w}_{2,OH}[HO]^{-} + k^{w}_{2,BrO^{-}}[HOBr]_{o}. \qquad (8)$$

Reactivity of hypobromite-containing systems from structurally different complexes VIII–XI are nearly the same (Table 4). This fact is not unexpected: amide fragments of the complexes are unreactive to the esters, and starting concentrations of

dibromobromates are usually insufficient to change the properties of media and affect the nucleophilicity of BrO^- anion.

BrO^- anion, being seven orders of magnitude less basic than hydroxide ion (pK_a 8.69 and 15.74, respectively [90]), reacts with the substrates under study at the rates similar to those for alkaline hydrolysis (Table 4). The magnitude of α-effect can be estimated from the ratio of the second-order rate constants $k_2^{\alpha-\text{nucl.}}/k_2^{\text{nucl.}}$, or alternatively, as a rate difference $\Delta = \lg k_2^{\alpha-\text{nucl.}} - \lg k_2^{\text{nucl.}}$, providing the acid dissociation constants of BrO^- anion, of conjugated acid of α-nucleophile and that of "normal" oxygen nucleophile are comparable in magnitude. From Brønsted relationship for arylate (alkoholate) ions [91], the reactivity of "normal" oxygen nucleophile – arylate ion, $pK_a^{ArOH} = pK_a^{HOBr} = 8.69$ – was calculated to be $2.5 \cdot 10^{-4}$ (NPDEPN), $2.3 \cdot 10^{-5}$ (NPDEP) and $3 \cdot 10^{-5}$ (NPOTos), $M^{-1}s^{-1}$.

Hence, the magnitude of α-effect defined as a ratio of second-order rate constants $k^{w}_{2,BrO^-}/k^{w}_{2,ArO^-}$, is about 600, 500 and 400 irrespective of the source of "active" bromine used. Similarly, an increase in reaction rate of ClO^- anion was found to be $k^{w}_{2,ClO^-}/k^{w}_{2,ArO^-} \geq 10^3$ ($pK_a^{HOCl} = pK_a^{ArHO} = 7.4$).

Table 4. Nucleophilic reactivity of hypobromite ion k^{w}_{2,BrO^-} toward NPDEPN, NPDEP, NPOTos; μ 1.0 (KCl), water, 25°C

Source of «active» bromine	k^{w}_{2,BrO^-}, $M^{-1}s^{-1}$		
	NPDEPN*	NPDEP*	NPOTos*
$Br_2 + H_2O$ (KOH)	0.156	0.010	0.017
VIII	0.116	0.011	0.0154
IX	0.120	0.011	0.015
X	0.13	0.010	0.015
XI	0.120		

*Rate constants of alkaline hydrolysis k^{w}_{2,OH^-}, $M^{-1}s^{-1}$ of NPDEPN, NPDEP and NPOTos are 0.15, 0.009 and 0.008, respectively [89].

As is evident from the above discussion, HOBr/BrO^- system provides a rapid decomposition of NPDEPN, NPDEP and NPOTos, thus supporting the considerable promise of such systems for decomposition of OPC. In practice, the use of bromine water is of little interest. Contrary, stable in storage, safe and easily manageable solid complexes VIII and X [89, 91] - can be recommended as highly efficient sources of "active" bromine.

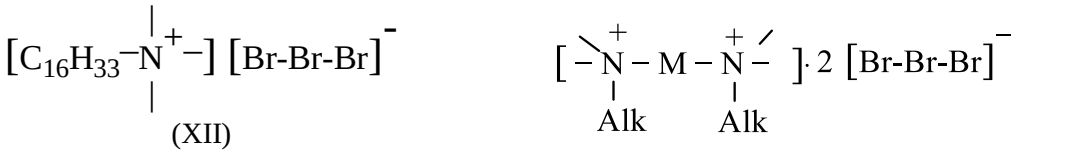
Dibromobromate surfactants in decomposition of ecotoxicants

Design of highly reactive reagents suitable for decomposition of ecotoxicants in water requires a search for versatile systems combining both oxidizing and nucleophilic properties. In addition, it is essential to provide high reaction rates and solubilization of the substrates only slightly soluble in water.

As was shown in numerous research works, the use of aqueous solutions of surfactants is the most efficient way to reach high reaction rates. This can result in design of highly selective supernucleophilic micellar systems with the desired

directionality in their action under “mild” conditions. Uniqueness of the surfactants with reactive counterion consists in that these reagents involve both reactive ion and micelle-forming surfactant.

Studies on stable bis(N,N-dialkylamide)hydrogen dibromobromates in decomposition of the esters of phosphoric, phosphonic and toluenesulfonic acids in the presence of cetyltrimethylammonium bromide made it possible to estimate catalytic effects of the latter [89] and, on the other hand, to support the feasibility of surfactant-based bromine complexes [91]. Cetyltrimethylammonium dibromobromate [XII] and first synthesized dibromobromates of ethanediyl-bis(dimethyldodecyl) ammonium (XIII), ethanediyl-bis(dimethyltetradecyl) ammonium (XIV) and butanediyl-bis(dimethyldodecyl)ammonium (XV) were studied in decomposition of 4-nitrophenyl esters of diethylphosphonic, diethylphosphoric and 4-toluenesulphonic acids.



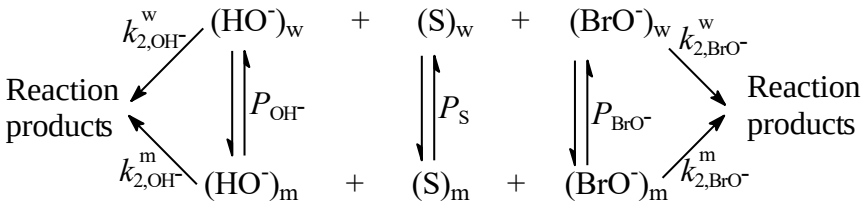
M= $(CH_2)_2$; Alk = $C_{12}H_{25}$ (XIII), $C_{14}H_{29}$ (XIV);
M= $(CH_2)_4$; Alk = $C_{14}H_{29}$ (XV)

Fig. 9. Structure of surfactants with reactive counterion.

Dicationic surfactants involve two hydrophobic moieties and two head groups bounded by the spacer fragments with different degree of rigidity. Compared with parent amphiphilic derivatives with one head group and one hydrocarbon chain, dicationic surfactants demonstrate lesser cmc, higher surface activity and wetting properties [42, 92–94]. Their structure modification allows one to obtain dicationic surfactant with two-fold increase in content of “active” halogen.

In aqueous solutions dibromobromate surfactants dissociate to give dibromobromate anion followed by the formation of, depending on pH, hypobromite anion BrO^- or hypobromous acid $HBrO^-$ and micellar pseudophase.

Decomposition of substrate (S) in micellar media is sufficiently complicated process involving two concurrent reaction routes – alkaline hydrolysis and interaction between substrate and hypobromite ion, both in water (w) and micellar pseudophase (m). The overall reaction can be presented as follows:



(9)

Partitioning of the substrate and reagents between water and micellar pseudophase is defined by coefficients $P_S = [S]_m/[S]_w$, $P_{BrO^-} = [BrO^-]_m/[BrO^-]_w$ and $P_{OH^-} = [HO^-]_m/[HO^-]_w$; k^w_{2,HO^-}, k^w_{2,BrO^-}, k^m_{2,HO^-} and k^m_{2,BrO^-} (all in $M^{-1}s^{-1}$) are the second-

order reaction rate constants describing nucleophilicity of hydroxide and hypobromite ions in water and micelles.

Figure 10 gives the observed reaction rate constants in decomposition of substrates in the presence of surfactant XIV plotted *vs* substrate concentration c_0. Representative plots of the apparent second-order rate constants ($k_{2,app.} = k_{obs.}/[BrO^-]$, $M^{-1}s^{-1}$) at a constant pH *vs* surfactant concentration in reaction of NPDEPN with hypobromite ion are shown in Fig. 11.

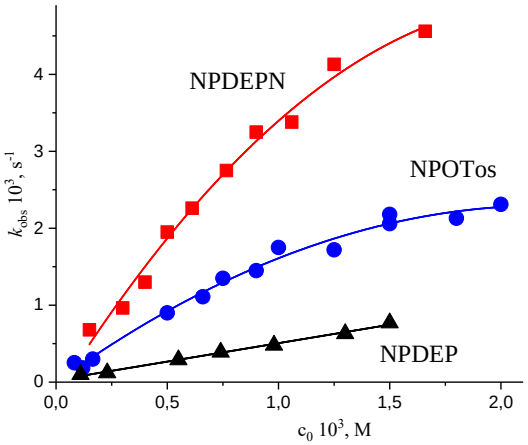


Fig. 10. Observed rate constants ($k_{obs.}$, s^{-1}) *vs* surfactant concentrations (c_0, M) for reaction with hypobromite ion generated from (ethanediyl-bis(dimethyltetradecy-l-ammonium) dibromobromate XIV). NPDEPN (pH 11.20); NPOTos (pH 11.50); NPDEP (pH 11.70); water, 25°C.

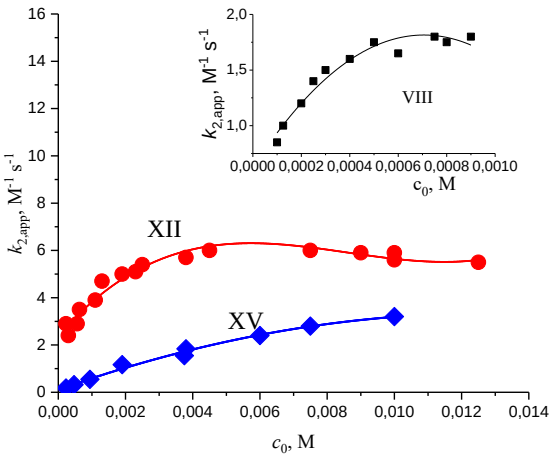


Fig.11. Rate constants $k_{2,app.}$ *vs* surfactant concentration for reaction of NPDEPN with hypobromite ion generated from dibromobromates XII and XV; VIII – in the presence of CTAB; water, pH 11.20, 25°C.

Taking into account the partitioning of substrate, hypobromite and hydroxide ions, decomposition of the esters in the presence of surfactants can be described in the framework of PPM [73–75]:

$$k_{obs.} = \frac{k^{m}_{2,OH^-} \cdot (1/V_m) \cdot K_{HO^-} \cdot K_S \cdot c + k^{w}_{2,HO^-}}{(1 + K_{HO^-} c) \cdot (1 + K_S c)} \cdot [HO^-]_0 + \frac{k^{m}_{2,BrO^-} \cdot (1/V_{m.}) \cdot K_{BrO^-} \cdot K_S \cdot c + k^{w}_{2,BrO^-}}{(1 + K_{BrO^-} c) \cdot (1 + K_S c)} \cdot [BrO^-]_0 \quad (10)$$

In equation (10) c, M is the concentration of micellized surfactant ($c = c_0 - \text{cmc}$), where c_0 is analytical concentration of surfactant; cmc, M is the critical micelle concentration; $c \cdot V_m$ and $(1 - c \cdot V_m)$ are the volume fractions of micellar and aqueous phase, respectively; $K_S = (P_S - 1) \cdot V_m$, $K_{BrO^-} = (P_{BrO^-} - 1) \cdot V_m$ and $K_{HO^-} = (P_{HO^-} - 1) \cdot V_m$, M^{-1} have dimensions of equilibrium binding constants of substrate, hypobromite and hydroxide ions, respectively; partial molar volume V_m, M^{-1} for surfactant XII is assumed to be 0.37 M^{-1}. In the case of surfactants XIII–XV hypobromite concentration is $[BrO^-]_0 = [BrO^-]_m + [BrO^-]_w = 2c_0$, concentration of micellized surfactant was estimated from cmc for dibromides of the corresponding dimeric surfactants – $5.0 \cdot 10^{-4}$ (XII), $5.0 \cdot 10^{-5}$ (XIII), and $8.0 \cdot 10^{-4}$ (XV) [29, 95]. Since the experimental partial molar volumes of surfactants XIII–XV are unavailable, their V_m was assumed to be 0.59 M^{-1} [79].

The data were treated without regard for alkaline hydrolysis of substrate (the first term in equation 10), since its contribution adds little to the observed reaction rates.

Physico-chemical parameters for decomposition of the esters by hypobromite ion in micellar pseudophase are given in Table 5.

Table 5. Reactivity of hypobromite ion in the presence of surfactants (water, 25°C)

Surfactant	$k^{m}_{2,\,BrO^-}$, $M^{-1}s^{-1}$	K_S, M^{-1}	K_{BrO^-}, M^{-1}	$c_{exp.}$	$\Delta_{exp.}$
NPDEPN					
*	0.17	150	12	0.006	26
XII	0.08	900	42	0.006	46
XIII	0.08	200	40	0.0015	10
XIV	0.05	300	55	0.0005	13
XV	0.085	210	45	0.0005	7
NPDEP					
*	0.008	200	26	0.013	35
XII	0.012	800	43	0.007	90
XIII	0.0035	220	40	0.0018	5
XIV	0.008	310	60	0.0005	8
XV	0.004	200	50	0.0005	4
NPOTos					
*	0.008	1600	13	0.0075	13
XII	0.016	1800	25	0.005	53
XIII	0.006	1900	45	0.0023	20
XIV	0.008	3000	60	0.0006	18
XV	0.0085	2200	50	0.001	20

*Bis(N, N-dimethylacetamide)hydrogen dibromobromate in the presence of CTAB;

$k^{w}_{2,\,BrO^-}$, $M^{-1}s^{-1}$, were 0.13, 0.01 and 0.017 for NPDEPN , NPDEP and NPOTos, respectively;

$\Delta_{exp.} = k^{m}_{obs,\,BrO^-} / k^{w}_{obs,\,BrO^-}$ at $c_{exp.}$, pH = const.

The observed reaction rates are differently affected by an increase in the length of alkyl substituent in surfactants XIII–XIV and spacer in XIV and XV. The substrates used are electrically neutral species, so hydrophobic interactions, progressively increased with the length of alkyl substituent, favors reagent (primarily ester) concentrating in micelles. An efficiency of substrate solubilization measured in terms of binding constant K_S, decreases in the order: K_S (XIV) > K_S (XV) ≈ K_S (XIII). The binding of nucleophilic reagent, hypobromite ion, by micelles XIII–XV is not too large and must be governed mainly by electrostatic interactions (K_{BrO^-} in Table 5). Within the limits of experimental error, K_{BrO^-} remains nearly the same.

Hydrophobic properties of substrate contribute considerably to the reaction rates in the presence of surfactants. It was shown that nucleophilic reactivity of hypobromite ion in decomposition NPDEPN, NPDEP and NPOTos in the presence of surfactants XII–XV is ordered like that in water. Due to more efficient solubilization of NPOTos in comparison with NPDEP, the observed rate constants at the same pH and $[BrO^-]_0$ (Fig. 10) in the presence of surfactants XIII–XV increase in the order: $k_{obs.}$(NPDEPN) > $k_{obs.}$(NPOTos) > $k_{obs.}$(NPDEP). With data from Table 5, the differences

in K_S for surfactants XIII and XV, defined as $K_S(\text{NPOTos})/K_S(\text{NPDEP})$, were calculated to be ≈ 10.

The observed reaction rate is a convenient experimental parameter for evaluation of the scope of micellar effects. Table 5 gives the ratios $\Delta_{exp} = k^{m}_{obs.}/k^{w}_{obs.}$ at a varied concentration of surfactants and hypobromite ion. In the series of the surfactants studied the observed increase in reaction rates vary from ~ 50 (NPDEPN, NPOTos) to ~ 90 (NPDEP) times (Table 5). Micellar catalysis normally depends on a number of the rate-controlling factors, primarily on nucleophilic reactivity and reagent concentrating in micellar pseudophase. Therefore, taking into account that the nucleophilicity of hypobromite ion in micellar pseudophase decreases 2–3-fold for all of the substrates, it is the effect of reagent concentrating which is mainly responsible for an increase in the observed reaction rates.

Supernucleophilic systems based on functionalized surfactants

Reactivity of micellar systems based on monomeric functionalized surfactants. Usually, only cationic surfactants are catalytically active in decomposition of acyl substrates (for nucleophilic substitution at electron-deficient centers, such as phosphorus, sulfur, and carbon), and acceleration of these reactions is determined by the effects of concentrating of substrate and reagent in micellar pseudophase [17, 50, 72–74, 82, 96, 97]. Although the presence of the micelles of the cationic surfactants can provide appreciable accelerations, their efficiency varies significantly with the binding of nucleophiles by the micellar pseudophase. One of the most efficient ways in design of surfactant-based supernucleophilic systems is their functionalization with nucleophilic fragments [98–109]. The binding of nucleophilic reagent is not necessary here. The attempts to design efficient surfactants functionalized with fragments like those in active center of hydrolytic enzymes cannot be considered as satisfactory. Design of surfactants involving imidazolium core, hydroxyl and thiol groups, and studies on their reactivity showed that the micellar effects in such surfactants are no more than ten-fold, i.e. considerably less than those in enzymatic reactions [99–103]. Therefore, functionalization of surfactant for the purpose of obtaining supernucleophilic systems requires somewhat different approach. It would be expected that the most efficient micellar systems can be, and this is the case, those combining the advantages of microheterogenous medium (high solubilizing ability toward substrate) and inorganic anionic α–nucleophile (abnormally high reactivity for electron-deficient centers – carbon, phosphorus and sulfur).

It was found that the most promising are the compounds functionalized by oximate, hydroxamate and amidoximate fragments. In this series oxime derivatives proved to be especially attractive. Firstly, an ease of structure modifications makes it possible to obtain oximes capable of decomposing ecotoxicants in a wide range of acidity of medium – from neutral to highly alkaline. Secondly, the most efficient antidotes, reactivators of acetylcholine esterase inhibited by organophosphorus compounds, were found among the compounds of this type. A search in this line is continued until now [14, 15, 27–30, 40, 51–63]. Undoubtedly the abnormally high reactivity of oximes is one of the factors determining their bioactive power [52–55, 57, 60, 62].

Comparison studies on nucleophilic reactivity of the functionalized surfactants based on imidazole (XVI–XX) and pyridine (XXI–XXV) involving α-nucleophilic functionality – aldoxime or ketoxime fragments (Fig. 12) – in decomposition of acyl substrates made it possible to establish the factors responsible for an increase in the observed reaction rates. Among these factors are nucleophilicity changes with structure and composition of co-micelles, basicity of oxime group, hydrophobic properties of substrate, etc. [44, 45, 51–63, 107].

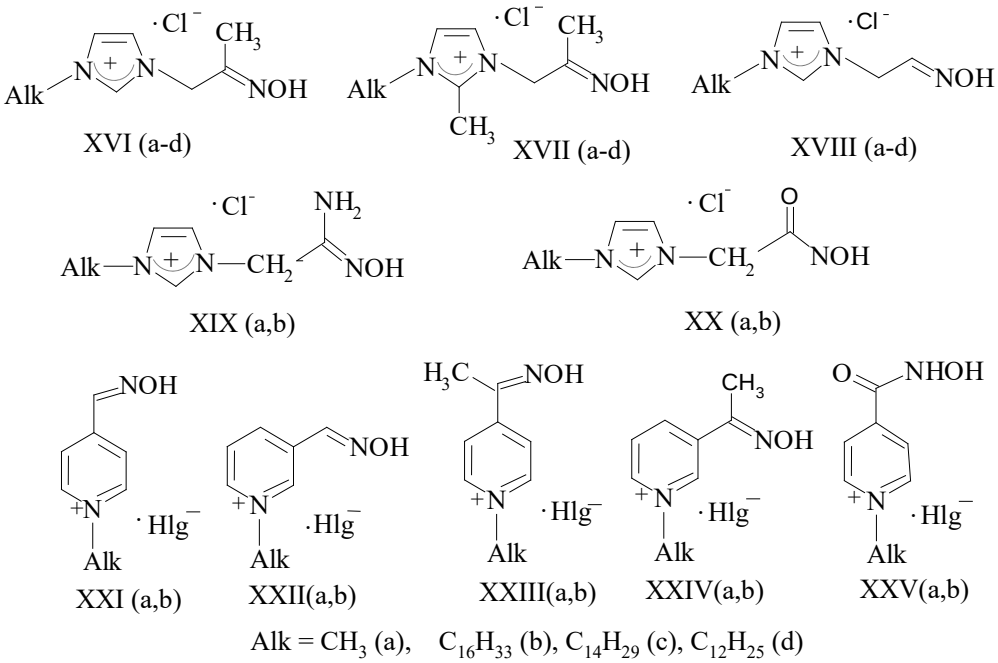
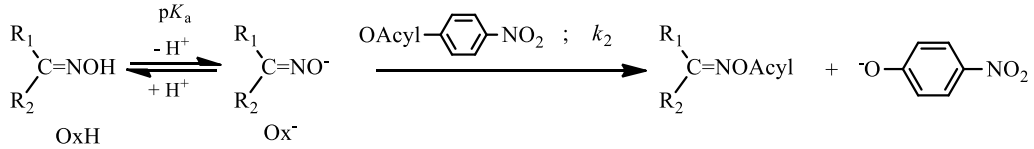


Fig. 12. Structure of functionalized monomeric surfactants on the basis of imidazole and pyridine.

Reactivity of the surfactants was compared with the nucleophilicity of the micelle-nonforming oximes (XVIa–XXVa). Nucleophilic attack of oximate fragment (Ox^-) of the functionalized surfactants and their micelle-nonforming methyl counterparts on electron-deficient centers of phosphorus and sulfur in substrates NPDEPN, NPDEP and NPOTos result in the formation of acylated oxime and 4-nitrophenolate ion [31, 44, 45] (Scheme 11):



(11)

where $R_1(R_2)C{=}NO^-$ is the corresponding fragment of surfactants XVI–XXV or oximes XVIa–XXa; Acyl = Et(EtO)P(O), $(EtO)_2P(O)$ or Tos.

Nucleophilicity of α-nucleophilic fragment in methyl counterparts XVIa–XXVa was determined from relationship «$k_2^{'} - k_2^{'} \cdot a_{H^+}$»:

$$k_2^{'} = \frac{k_{obs.} - k_{HO^-}^{w} \cdot a_{HO^-}}{[OxH]_0} = k_2^{w} - \frac{k_2^{'} \cdot a_{H^+}}{K_a}, \qquad (12)$$

where $[OxH]_0$, M is the analytical concentration of oxime; a_{OH^-} and a_{H^+} is the activity of hydroxide anion and hydrogen ion, respectively; $k_{obs.}$, s^{-1} is the observed reaction rate; k_2^w and $k_{HO^-}^w$, $M^{-1}s^{-1}$ is the second-order reaction rate describing the nucleophilicity of oxime and hydroxide ion, respectively; K_a is the acid dissociation constant of oxime [44, 45, 51–63].

In the presence of functionalized surfactants XVI–XXI the reaction rate is increased with pH at a constant analytical concentration of the surfactant (Fig. 13) and with the surfactant concentration at a constant pH (Fig. 14).

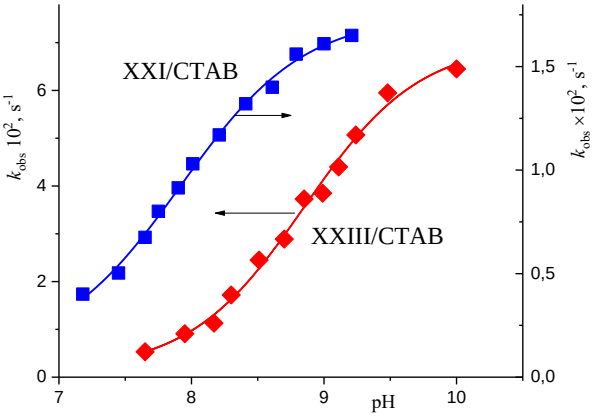


Fig.13. pH-dependence for interaction of comicellar systems XXI / CTAB and XXIII / CTAB with NPDEPN; c_0 0.006 M, χ 0.25, 0.01 M borate buffer, 25°C.

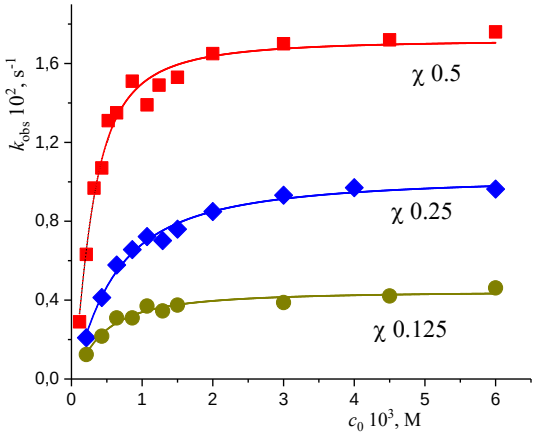


Fig.14. Concentration plots for interaction of comicellar systems XXI / CTAB with NPOTos; pH 10.5, 0.01 M borate buffer, 25°C.

In the first case an increase in reaction rate supports the validity of equation 13, and, hence, the conclusion that oximate ion is the reactive form; the second case is an evidence for ever increasing substrate binding and concentrating of the substrate in micellar pseudophase. In the most complete form the reaction scheme can be presented as follows:

$$\begin{array}{lcl} (S)_m + Ox^- & \xrightarrow{k_2^m} & \text{Reaction products} \\ \rightleftarrows & & \\ (S)_w + OH^- & \xrightarrow{k_{OH}^w} & \text{Reaction products} \end{array} \qquad (13)$$

Taking into account equilibrium partitioning of substrate between aqueous and micellar phase ($P_S = [S]_m / [S]_w$), the observed rate constant can be expressed as [44, 45, 73–75]:

$$k_{obs.} = \frac{\chi(k_2^m / V_m)K_S c + k_{HO^-}^w \cdot a_{HO^-}}{1 + K_S c} \cdot \frac{K_{a,app.}}{K_{a,app.} + a_{H^+}}, \qquad (14)$$

where $K_{a,app.}$ is an apparent acid dissociation constant of the functionalized fragment. Since the functionalized surfactants are only slightly soluble in water, the micellar effects of such surfactants were studied in comicellar system "functionalized surfactant (FD) – CTAB" at a varied fraction of the former ($0,1 < \chi \leq 1$, where χ is the mole

fraction of the surfactant). In the most cases concentration plots were obtained at a pH where the functionalized fragment is completely ionized (Figs. 13, 14).

For acyl transfer reactions, the reactivity of oximes – typical α-nucleophiles – cannot be described by linear Brønsted relationship [31, 81, 111]. For oximes with $pK_a \approx 8.0–9.0$ the corresponding plots flatten out and the sensitivity of the reaction series to the basicity of the nucleophile (β_N) changes from $\beta_N \approx 0.4–0.6$ (at $pK_a \leq 8.0–9.0$) to $\beta_N \approx 0–0.1$ (at $pK_a \geq 8.0–9.0$). Similar change in β_N was observed for interaction of acyl substrates with "normal" oxygen reagents (alcohols and phenols with an inflection point at $pK_a \geq 12.0$ [112–118]) as well as with neutral and anionic nitrogen compounds (inflection point at $pK_a \approx 10.0–11.0$ [116]). It is remarkable that their methyl counterparts XVIIa–XXVIIa (like XVIa in [44, 45, 52, 55]) behave without any sign of being distorted (for example, due to a charge "effect") and the points for these oximes fall on the corresponding plots (Fig. 15).

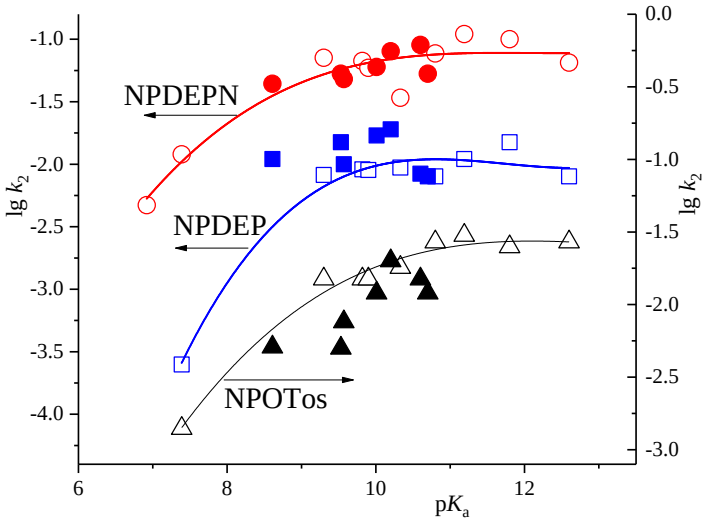


Fig. 15. Brønsted plots for interaction of micelle-nonforming oximes (open symbols) with NPDEPN, NPDEP, and NPOTos; filled symbols denote points for methyl counterparts XVIa–XVIIIa and XXIa–XXIVa; points for the other oximes were taken from [31, 52]).

Nonlinearity of Brønsted plots for the reactants of diverse nature – oximate, alkoholate, phenolate ions, and neutral and anionic nitrogen compounds – can be assigned to a number of factors including structure changes in the transition state, or energetically unfavorable solvation effects whose contribution becomes progressively more significant with an increase in the basicity of nucleophile. Large body of evidence [111–115] suggests that it is the differences in solvation states of low- and high-basicity oximes appear to be responsible for the observed nonlinearity of Brønsted relationships in reactions of oximate ions with acyl substrates.

As evidenced by $\Delta_1 = k_2^m / k_2^w$ in Table 6, nucleophilicity of oximate fragments in functionalized surfactants is slightly higher than that in their methyl counterparts. A somewhat different behavior was detected in reactions of NPDEPN with oximate group of functionalize surfactant XVII and reaction of NPDEP and NPOTos with XXI. In the first reaction the second-order rate constant increases about six-fold, whereas a decrease in ratios k_2^m / k_2^w (see the corresponding values of Δ_1 in Table 6)

is observed for the other two. Such discrepancies in the reactivity may be caused by differences in localization of substrate and oximate fragment in functionalized surfactant [105, 106]. In most reaction series an increase in nucleophilicity should be attributed not only to favorable orientation of the ester relative to functionalized fragment in micellar pseudophase, but also to the influence of micellar medium on desolvation of oximate ion.

Table 6. Micellar effects of functionalized surfactants in decomposition of NPDEPN, NPDEP and NPOTos

Surfactant	α_S*	Substrate											
		NPDEPN				NPDEP				NPOTos			
		χ**	Δ_1	Δ_2	Δ***	χ**	Δ_1	Δ_2	Δ***	χ**	Δ_1	Δ_2	Δ***
XVIb	<<1	1.0	1.8	520	940	1.0	0.95	560	530	1.0	2.1	6600	13860
	≈ 0.9	1.0	1.8	52	94	1.0	0.95	56	53	1.0	2.1	660	1390
XVIIb	<<1	1.0	6.4	400	2560	1.0	1.25	320	400	1.0	3.3	4400	14520
	≈ 0.9	1.0	6.4	40	256	1.0	1.25	32	40	1.0	3.3	440	1450
XVIIIb	<<1	1.0	2.3	480	1100	1.0	1.3	360	470	1.0	1.7	6000	10200
	≈ 0.9	1.0	2.3	48	110	1.0	1.3	36	47	1.0	1.7	600	1020
XXIb	<<1	0.5	1.0	500	500	0.5	0.25	475	120	0.25	0.3	6750	2030
	≈ 0.9	0.5	1.0	50	50	0.5	0.25	48	12	0.25	0.3	675	203
XXIIb	<<1	0.25	3.6	400	1440	0.5	0.9	375	340	0.5	3.2	7000	22400
	≈ 0.9	0.25	3.6	40	144	0.5	0.9	38	34	0.5	3.2	700	2240
XXIIIb	<<1	0.5	4.2	530	2230	0.5	1.7	500	850	0.25	1.3	7500	9750
	≈ 0.9	0.5	4.2	53	223	0.5	1.7	50	85	0.25	1.3	750	975
XXIVb	<<1	0.25	3.2	630	2020	0.25	0.9	625	560	0.25	1.25	7500	9380
	≈ 0.9	0.25	3.2	63	202	0.25	0.9	63	57	0.25	1.25	750	938

*Fraction of substrate in micellar pseudophase.

**Mole fraction of functionalized surfactant in comicelles with CTAB.

***From equation $\Delta = \Delta_1 \cdot \Delta_2 = (k_2^m / k_2^w) \cdot \chi \cdot P_S \cdot c / \{[OxH]_0^{MeA} \cdot (1 + K_S \cdot c)\}$, where Δ_1 and Δ_2 correspond to the change in reactivity of oximate fragment and the effect of substrate concentrating, respectively [52].

The similar tendency in influence of acid-base properties on the reactivity of functionalized fragment was first detected in our laboratory for oximate surfactants XVIb–XVIIIb and XXIb–XXIVb (Fig. 16). As in the case of micelle-nonforming oximes [31, 81, 110], functionalized surfactants with $pK_a \geq 8.5$–9.0 react with NPDEPN, NPDEP and NPOTos at nearly the same rates with $\beta_N \rightarrow 0$. At $pK_a \leq 8.5$–9.0 the reactivity of functionalized surfactant decreases, i.e. Brønsted plot is nonlinear and $\beta_N > 0$. Reliable estimation of β_N on the descending portion of the Brønsted plots can be carried out using extended set of surfactants with $pK_a \leq 9.0$. Similarity in the effects of acid-base properties on nucleophilicity of oximes in water (Fig. 15) and oxime group in functionalized surfactants XVIb–XVIIIb and XXIb–XXIVb (Fig. 16) in acyl transfer makes it possible to give some assumptions on the role of the microenvironment in micelles of functionalized surfactants and development of supernucleophilic systems with the required reactivity.

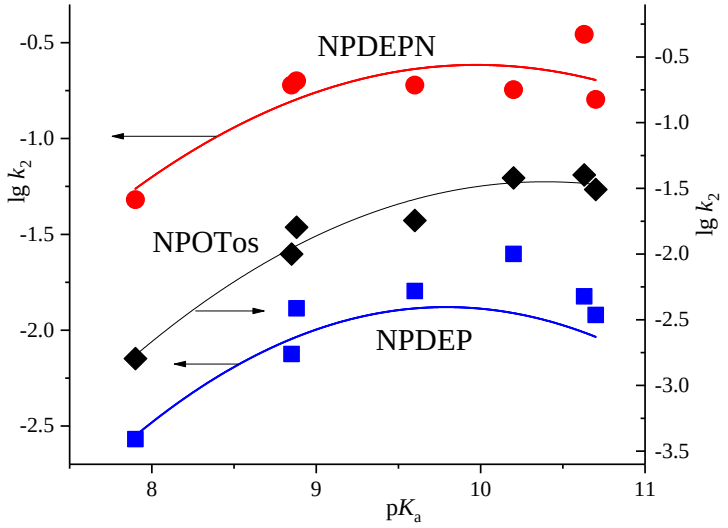


Fig. 16. Brønsted plots for reactions of functionalized surfactants with NPDEPN, NPDEP, and NPOTos [52].

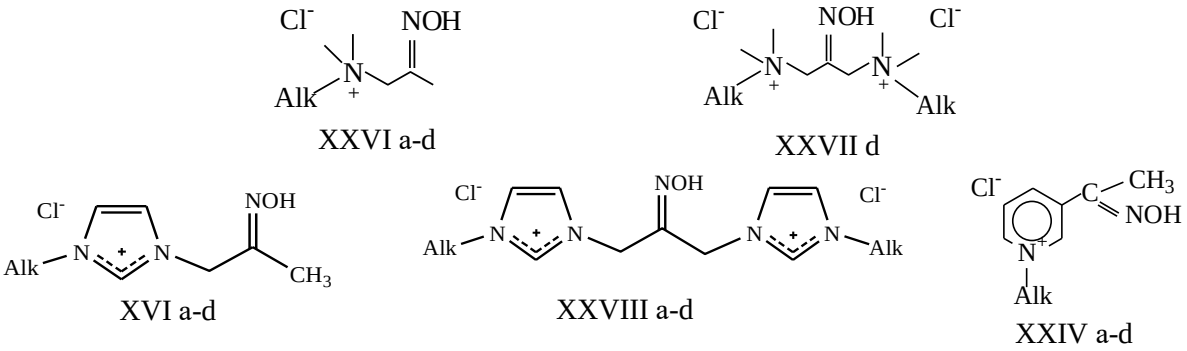
Nonlinearity of Brønsted plots and the fact that the inflection points are observed at similar pK_a values of oxime and oxime fragment in functionalized surfactant clearly show that microenvironmental effects in micelles are much like those in water, and desolvation effects in functionalized fragment, as is the case in micelle-nonforming oximes, are also essential here. Therefore, design of surfactant-based supernucleophilic systems with oxime functionality for decomposition of ecotoxicants under "mild" conditions requires surfactants with p$K_a \approx 7.0–9.0$.

A comparison of Δ_1 and Δ_2 from Table 6 suggests that the effect of substrate concentrating in micelles and comicelles is the main factor responsible for micellar effects in the monomeric functionalized surfactants.

In practice, half-reaction time ($\tau_{1/2}$, s) is a characteristic useful in estimating the efficiency of decomposition of ecotoxic acyl substrates. Half-reaction times are dependent on the nature of substrate, their minimum values were calculated to be 1s (NPDEPN), 14s (NPDEP) and 9s (NPOTos), which fully meet the requirements for active components of the formulations suitable for decomposition of organophosphorus compounds. Therefore, the oxime-functionalized surfactants are powerful supernucleophilic reagents, which can provide ~ 10^2–10^4-fold acceleration in decomposition of acyl substrate as compared to their methyl counterparts. Their efficiency in decomposition of acyl substrates not only highly competitive with, but also outperform currently existing functional surfactants of other types.

Reactivity of micellar systems based on dimeric functionalized surfactants. Surfactants with α-nucleophilic functionalities – hydroxamate, amidoximate and oxymate – combine both abnormally high reaction rates in acyl transfer and efficient solubilzation of the substrates slightly soluble in water [60, 61, 118, 122]. Between these compounds oxime-functionalized surfactants are the most attractive for supernucleophilic systems design. Firstly, structure variations in the surfactants make it possible to obtain compounds with pK_a of oxime functionalities close to physiological pH [60, 61, 121]. Secondly, the reactivity of oximate fragment in the surfactants, as with their micelle-nonforming counterparts, directly depends on its acid-base properties [19, 55,

60, 61]. Inflection points in Brønsted plots fall into the same range of pK_a ≈ 8.5–9.5. Already known interrelation between the nucleophilic reactivity (k_2^m and k_2^w, $M^{-1}\cdot s^{-1}$) and acid-base properties of oxime group simplifies design of the surfactants with desired nucleophilicity and pK_a. Thirdly, since physico-chemical properties of micellar pseudophase depend largely on the nature of the head group [52, 53], the structure of the latter is one of the main factors responsible for micellar effects. And, finally, since substrate concentrating in the micellar pseudophase makes dominating contributions to the observed reaction rate, the hydrophobic properties of functionalized surfactants become essential for micellar effects [54, 57, 58, 62, 121, 122].



Alk = CH_3 (a), $C_{16}H_{33}$ (в), $C_{14}H_{29}$ (c), $C_{12}H_{25}$ (d),

Fig. 17. Structure of functionalized monomeric and dimeric surfactants.

While the influence of the functional fragment, hydrophobicity of surfactant and substrate on micellar effects can be considered as being well-established, the effects of the nature of cationic center in the head group, and hydrophobic properties require further investigations.

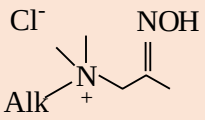
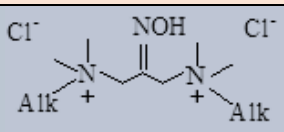
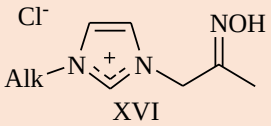
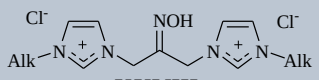
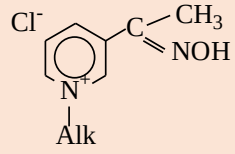
Comparative analysis of micellar effects at a varied nature of cationic fragment in the head group and the length of hydrocarbon tail in micellar and comicellar systems XVI, XXIV and XXVI–XXVIII, presented further. It should be noted that studies on the effects of hydrophobic properties is also of pragmatic interest since it makes possible to optimize the structure of surfactant with due regard for the nature of alkyl substituent. Undoubtedly, the appropriate selection of structure modifications in surfactant requires a close examination of changes in a number of physico-chemical parameters of functionalized surfactants in aqueous solutions: solubilization efficiency of substrate, nucleophilic reactivity of oximate group in surfactant, aqueous solubility of surfactants, cmc, etc.

Regularities in the kinetics of 4-nitrophenyl diethylphosphonate decomposition in micelles and comicelles. The main regularities in decomposition of esters, NPDPEN included, both in comicells and solutions involving functional dimeric surfactants are similar to those discussed above for monomeric surfactants. Regularities in behavior of the observed pseudo-first order rate constants are well fitted by equation 14 [73, 75].

Physico-chemical parameters used in description of NPDEPN hydrolysis in functionalized surfactants micelles and comicelles FD/CTAB are given in Table 7.

An important property of micellar systems is their ability to solubilize a wide diversity of compounds. Solubilization is closely associated with hydrophobic features of surfactant such as the nature of the head group and number of methylene

Table 7. Reactivity of oximate ion (k_2^m) in decomposition of NPDEPN in micellar and comicellar systems, and physico-chemical characteristics of surfactants (p$K_{a,\,app.}$, K_S, cmc) for compounds XVI, XXIV and XXVI–XXVIII

Compound	Alk	p$K_{a,\,app.}$*	χ**	k_2^m, $M^{-1}s^{-1}$***	K_S, M^{-1}***	cmc, M****
 XXVI	XXVIb $C_{16}H_{33}$	10.12 (sp.), χ 1.0) 10.33 (kin.), χ 0.125)	0.1 0.125	0.05 0.08	115 160	$< 3 \cdot 10^{-5}$
	XXVIc $C_{14}H_{29}$	10.25 (sp.), χ 1.0 10.20 (kin.), χ 0.125	0.1 0.125	0.1 0.1	160 260	$3 \cdot 10^{-5}$ (kin.)
	XXVId $C_{12}H_{25}$	10.15 (sp.), χ 1.0 10.23 (sp.), χ 0.125	0.1 0.125	0.13 0.13	70 60	$2 \cdot 10^{-3}$ (kin.) $2 \cdot 10^{-4}$ (kin.)
 XXVII	XXVIId $C_{12}H_{25}$	9.44 (sp.), χ 1.0 9.49 (sp.), χ 0.125	1.0 0.125	0.08 0.08	72 93	$4 \cdot 10^{-4}$ (kin.) $4 \cdot 10^{-4}$ (kin.)
 XVI	XVIb $C_{16}H_{33}$	10.7 (kin), χ 1.0 10.39 χ 1.0 10.44 χ 0.125	1.0 0.125	0.16 0.16	260 364	$2.5 \cdot 10^{-4}$ (kin.) $< 2.6 \cdot 10^{-4}$ $6.4 \cdot 10^{-4}$
	XVIc $C_{14}H_{29}$	10.60 χ 1.0 10.37 χ 0.125	1.0 0.125	0.13 0.16	130 260	$4.2 \cdot 10^{-4}$ (kin.) $8.4 \cdot 10^{-3}$
	XVId $C_{12}H_{25}$	10.50 (sp.), χ 1.0 10.10 (kin.), χ 1.0 10.29 (sp.), χ 0.125	1.0 0.5 0.125	0.09 0.12 0.11	91 91 155	$3 \cdot 10^{-3}$ (kin.) $2.8 \cdot 10^{-3}$
 XXVIII	XXVIIIb $C_{16}H_{33}$	9.0 (kin.), χ 1.0 8.9 (sp.), χ 1.0 8.7 (sp.), χ 0.125	1.0	0.20	250	$< 2 \cdot 10^{-5}$
	XXVIIIc $C_{14}H_{29}$	8.9 (kin.), χ 1.0 8.,8 (sp.), χ 1.0 8.9 (sp.), χ 0.125	1.0	0.20	250	$< 2 \cdot 10^{-5}$
	XXVIIId $C_{12}H_{25}$	8.8 (kin.), χ 1.0 8.9 (sp.), χ 1.0 8.9 (sp.), χ 0.125	1.0 0.125	0.20 0.17	155 160	$< 2 \cdot 10^{-4}$ $1 \cdot 10^{-4}$
 XXIV	XXIVb $C_{16}H_{33}$	9.29 (sp.), χ 1.0	0.25 0.125	0.22 0.23	250 250	$< 3 \cdot 10^{-4}$ $< 3 \cdot 10^{-4}$
	XXIVc $C_{14}H_{29}$	9.63 (sp.), χ 1.0	0.5	0.23	200	$3 \cdot 10^{-4}$ (kin.)
	XXIVd $C_{12}H_{25}$	9.90 (sp.), χ 1.0	1.0 0.125	0.18 0.20	180 180	$5 \cdot 10^{-4}$ (kin.

*Spectrophotometric (sp.) or kinetic (kin.) measurements;
**Mole fraction of functional surfactant in comicelles FD/CTAB.
***Accurate within 10%.
****From kinetic data.

units in alkyl substituent. In the case of dimeric surfactants, the length and structure of the bridge chain (spacer) is also should be taken into account [123]. One of the most important characteristics of micelle formation is a critical micelle concentration

(cmc). Since cmc depends on a number of factors (length of alkyl substituent, the presence of polar and ionogenic groups and influence of electrolytes used in maintenance of pH in the system), in the most cases preference was given to the cmc determined by kinetic method.

Acid dissociation constants of oxime group ($pK_{a,app.}$) were determined by spetrophotometric and kinetic methods [51–63]. The values of $pK_{a,app.}$ are slightly affected by variations in the length of alkyl substituent in the head moiety of monomeric and dimeric surfactants (Table 8) whereas an introduction of the second electron-deficient substituent with the formation of dicationic surfactant results in significant decrease in $pK_{a,app.}$ (Table 7), i.e. compounds XXVII and XXVIII are more strong acids than oximes XXVI and XVI.

Fraction χ variations do not change $pK_{a,app}$ sufficiently in the case of dimeric surfactants; for monomeric surfactants, influence is not regular (see Table 7), and data rationalization is not obvious.

There is principal difference: for non-functionalized cationic surfactants, changes in nucleophile $pK_{a,app}$ are considered as result of changes in binding of neutral and anionic forms with micelle; in a case of functionalized cationic surfactants, changes in nucleophile $pK_{a,app}$ are connected with differences in micelle structure, and with specific features of proton transfer into micelle surface layer.

The observed rate constants increase with increasing fraction χ of functionalized surfactant in comicelles FD/CTAB. Since the functionalized surfactants serve a dual function, namely, participate in formation of micellar pseudophase and, on the other hand, act as a functionalized reagent, the concentration of oximate ion and, hence, reaction rate increases with increased fraction of functionalized surfactant.

Reactivity, binding efficiency and micellar effects in decomposition of 4-nitrophenyl diethyl-phosphonate. Influence of hydrophobic "tail". Concentration plots in Figs. 18 and 19 demonstrate an influence of hydrophobicity of alkyl substituent and the nature of head group on the efficiency of micellar catalysis in micelles and comicelles FD/CTAB. Since $k_{obs.}$ for OMS were determined at a constant pH, their comparison will be more illustrative in terms of ratios $k_{obs.}/\alpha$, where α is the ionization degree of oxime group.

Effects of the length of alkyl "tail" on $k_{obs.}/\alpha$ ratios for tetraalkylammonium surfactants are different from those for compounds with imidazole and pyridine core [52, 58, 60]. In the two latter cases an expected regular change in reaction rate is observed at a varied number of methylene units in alkyl substituent: $k_{obs.}/\alpha$ for XVId < XVIc < XVIв; $k_{obs.}/\alpha$ XXVIIId < XXVIIIc < XXVIIIв, and XXIVd < XXIVc < < XXIVв (Figs. 18, 19). In this case the micellar effects of dimeric surfactants XXVIIIc in decomposition of NPDEPN is markedly higher than those for their monomeric counterparts. It looks reasonable to suppose that, as distinguished from monomeric surfactants and their dimeric counterparts at Alk = const, insertion of more water molecules and, hence, the formation of more loosely packed micellar structures does not occur here.

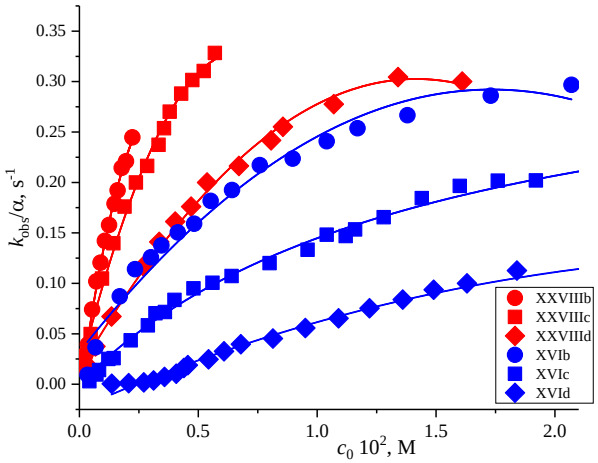


Fig. 18. $k_{obs.}/\alpha$, s^{-1} for decomposition of NPDEPN *vs* surfactant concentration in micelles XVI and XXVIII; χ 1.0; water, 25°C.

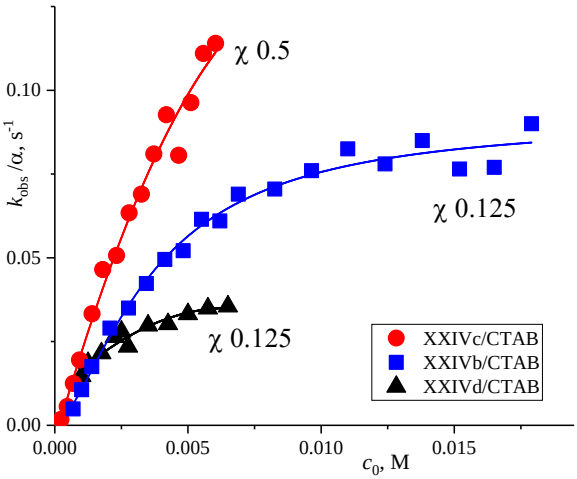


Fig.19. $k_{obs.}/\alpha$, s^{-1} for decomposition of NPDEPN *vs* analytical surfactant concentration in comicelles XXIV/CTAB; water, 25°C.

An influence of alkyl tail in tetraalkylammonium surfactants on micellar effects is not so distinct as for pyridine and imidazole containing compounds. Firstly, the micellar effects in surfactants XXVI (b-d) are nearly the same; secondly, those for dimeric surfactant XXVII are markedly less (down to two-fold) than in their monomeric counterparts. In addition, micellar effects depends on a number of factors such as nucleophilicity of the functional fragment, "shift" in $pK_{a,\,app.}$ and reagent concentrating in micellar pseudophase.

Binding constants K_S (Table 7) may serve as a measure of reagents concentrating. For electrically neutral substrate NPDEPN the hydrophobicities of both substrate itself and functionalized surfactant contribute significantly to K_S. Less efficient binding of NPDEPN by OMS based on XXVII as compared with that of XXVIIIb exerts diminishing effect on its concentrating in micelles and comicelles, thus reducing the observed reaction rates. Near two-fold decrease in binding constant of NPDEPN for XXVIb and XXVIIIb appears to be indicative of changes in the region of ester localization (near the surface of micelle). This hypothesis requires further studies on substrates with other hydrophobic properties. Nevertheless, there is little doubt that substrate concentrating is one of the controlling factors responsible for efficiency of micellar "catalysis".

And, finally, the nucleophilicity of oximate fragment needs more detailed consideration. Data from Table 7 unambiguously show that k_2^m depends only slightly on the length of alkyl "tail" and comicellar composition. This appears to be due to a close similarity in changes of medium properties in the micellar and comicellar regions where the reaction proceeds. Moreover, in spite of decrease in apparent acid dissociation constants of functionalize fragment going from monomeric XVI to dimeric XXVIII surfactants, k_2^m vary only slightly. Such behavior agree with our previous observations that, as in water, Brønsted relationships for decomposition of acyl substrates in micelles and comicelles involving imidazole, pyridine and tetraalkylammonium moieties are nonlinear with an inflection point at $pK_{a,\,app.} \approx 8.5–9.0$ [50–55, 58]. Negative deviation of XXVIId from Brønsted plot in Fig. 20 is consistent with low values of K_S and k_2^m (Table 7), i.e. there is an unidirectional

action of two factors – decrease in substrate concentrating in micelles and nucleophilic reactivity [50–55, 58].

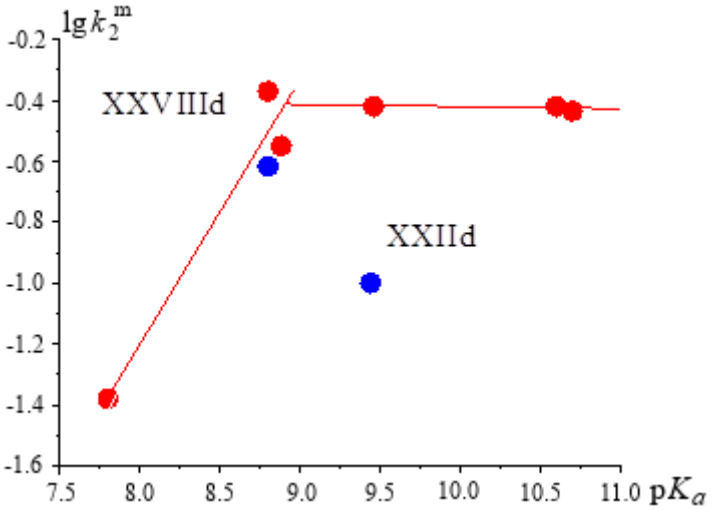


Fig. 20. Brønsted plot for decomposition of NPDEPN by oxime surfactants XXVIId and XXVIIId (solid circles); the remaining points (open circles) were taken from [110].

Data on k_2^m and K_S gives no straightforward information on the scope of micellar effects of the functional surfactants under study. At the same time the differences in the trends of the observed reaction rates in water (micelle-nonforming oximes with pK_a ≈ ≈ p$K_{a,\ app.}$) and micellar systems make it possible to draw some conclusions concerning these factors, and possible directions of structure modifications in functionalized surfactants that would be the most effective. Thus, half-reaction times in OMS on the basis of XVIId and XXIVd were found to be 13 and 9 s, whereas those for their methyl counterparts are 760 and 1400 s; i.e. an increase in reaction rate is about 60 and 150 times, respectively. Maximum acceleration is detected for imidazolium and pyridinium surfactants, whereas minimum acceleration is observed for tetraalkylammonium compounds (Fig. 21).

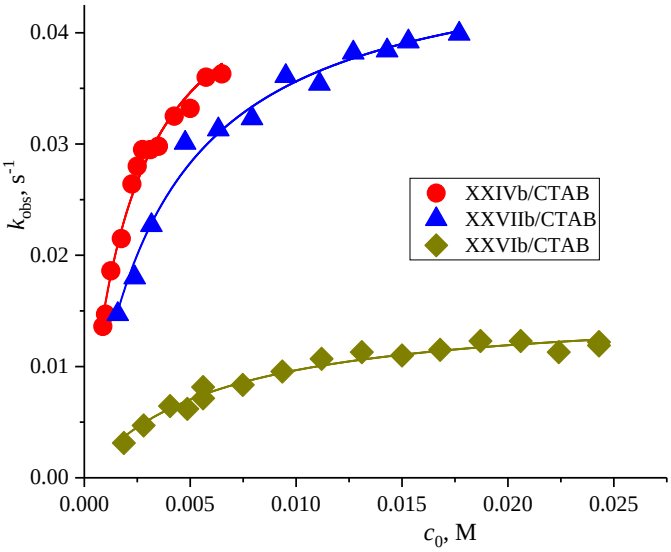


Fig 21. Observed rate constants $k_{obs.}$, s^{-1} *vs* total concentration of surfactants for decomposition of NPDEPN in comicelles at pH > p$K_{a,\ app.}$; χ 0.125; water, 25°C.

However, some consideration should be taken into account. **Firstly**, an increased length of alkyl substituent gives rise to significant increase in water solubility of functionalized surfactants, so that the micellar effects in the systems with no inert cosurfactant (CTAB) can be determined only for compounds XXVId and XXIVd. Table 8 gives the data on low soluble surfactants at their fraction χ 1.0. Unfortunately, experimentally accessible concentration range for such surfactants is extremely narrow. In this respect pyridinium and tetraalkylammonium surfactants are behind imidazolium surfactants whose solubility even for surfactant XVIb with Alk = $=C_{16}H_{33}$) is plenty large enough for their study without the use of comicellar systems. A decrease in fraction of functionalized surfactant in comicelles results in proportional decrease in the observed reaction rates in decomposition of substrate. **Secondly**, for all surfactants under study the substrate concentrating adds considerably to the observed reaction rates. Water solubility is one of the most important properties, since water can be efficiently used as a solvent to fit the requirements of "green" chemistry.

Micellar effects in functionalized tetraalkylammonium surfactants. Influence of substrate structure. Studies on the reactivity of dimeric functionalized surfactants XXVII and XXVIII in decomposition of NPDEPN showed that the nucleophilicity of XXVII, in spite of higher basicity, is lower than that of XXVIII [53–55]. Bronsted plots for functionalized surfactants in phosphonyl transfer demonstrate that the point for XXVII undergo significant negative deviation whereas that for XXVIII obeys the Bronsted relationship (Fig. 20). Whether this phenomenon is general or specific of, and peculiar to 4-nitrophenyl diethylphosphonate? Some considerations regarding the reactivity of tetraalkylammonium surfactant XXVII in phosphoryl (NPDEP) and sulfonyl (NPOTos) transfer are given below.

Since the solubility of the functionalized tetraalkylammonium surfactant proved to be too low, an estimation of the micellar effects and their comparison were carried out with comicellar systems "functionalized surfactant – CTAB". Effects of comicellar systems XXVII/CTAB on reaction rates in decomposition of substrates NPDEPN, NPDEP and NPOTos are similar to those established previously for micellar and comicellar systems involving oximate functionality [45, 52–55].

All concentration and pH dependences are well fitted by pseudophase model (Eq. 14). Table 8 gives $pK_{a,\,app.}$, k_2^m and other parameters for decomposition of esters in the systems involving XXVIId and XXVIIId in micellar pseudophase. The values of cmc were determined from kinetic data [45; 55].

As with NPDEPN [55], the behavior of surfactants XXVIId and XXVIIId differs markedly. Nucleophilic reactivity of XXVIId is lower than that of XXVIIId both in decomposition of NPOTos [k_2^m (XXVIIId) / k_2^m (XXVIId) ≈ 5] and NPDEP [k_2^m (XXVIIId) / k_2^m (XXVIId) ≈ 2.5].The similar ratios of rate constants were detected in their reaction with NPDEPN [k_2^m (XXVIIId) / k_2^m (XXVIId) ≈ 2, Table 8]. As evidenced by the data in Figs. 22 and 23, the points for XXVIId in Brønsted plots for decomposition of NPDEP and NPOTos by functionalized surfactants, as with NPDEPN, exhibit negative deviations. The binding constants of substrates (K_S) for comicelles on the basis of surfactant XXVIId are lower than that for XXVIIId, and the

observed decrease is nearly independent of the nature of substrate (Table 8). Deviations in nucleophilicity of oximate fragment in XXVIId in ethers decomposition can be attributed to decreased electron density at nucleophilic center as a result of efficient electrostatic interaction with one of the cationic centers of the molecule [55]. This kind of interaction is less effective in surfactant XXVIIId due to planarity of imidazole rings and packing features of surfactant molecules in micelle formation [86, 123]).

Table 8. Physico-chemical properties and nucleophilic reactivity of surfactants XXVIId and XXVIIId in decomposition of NPDEPN, NPDEP and NPOTos; 0.01 M borate buffer, 25°C

Surfactant	p$K_{a,\,app.}$	χ	pH	k_2^m / V_M, s^{-1}	k_2^m, $(M^{-1}\cdot s^{-1})$	K_S, M^{-1}	cmc, M
NPDEPN							
XXVIId	9.44 (χ 1.0) 9.49 (χ 0.125)	0.5 0.25 0.125	10.45 10.46 10.46	0.19 0.20 0.19	0.076 0.080 0.076	72 74 93	0.0004 0.0003 0.0003
XXVIIId	8.9 (χ 1.0) 8.9 (χ 0.125)	1.0 0.125	10.00 10.51	0.40 0.43	0.20 0.17	155 160	0.00005 0.0001
NPDEP							
XXVIId	9.4 (χ 1.0) 9.5 (χ 0.125)	0.5 0.25	10.46 10.40	0.0073 0.0075	0.0029 0.0030	90 90	0.0004 0.0003
XXVIIId	8.9 (χ 1.0) 8.9 (χ 0.125)	1.0	10.94	0.034	0.017	175	0.00007
NPOTos							
XXVIId	9.4 (χ 1.0) 9.5 (χ 0.125)	0.5 0.25 0.125	10.65 10.46 10.40	0.018 0.017 0.017	0.0072 0.0068 0.0068	820 520 570	0.0003 0.0003 0.0003
XXVIIId	8.9 (χ 1.0) 8.9 (χ 0.125)	1.0	10.99	0.031	0.016	1700	0.00002

As for binding constants, geometry and electrostatics are hardly satisfactory enough for explanation on the differences of. A 2 - 5-fold decrease in binding constants of substrates by comicelles XXVIId/CTAB as compared to similar systems involving XXVIIId (Table 8) irrespective of their hydrophobic properties is evidence for changes both in the localization of less hydrophobic esters NPDEPN, NPDEP (close to the micellar surface) and significantly more hydrophobic ester NPOTos (close to the micellar core). This observation is unexpected since the formation of micelles usually proceeds with changes at the micellar surface rather than in micellar core [63, 73, 123]. This interesting object (comicelles of XXVIII/CTAB) deserve for detailed structural studies.

To summarize, the results suggest that (i) structural changes of cationic center in the head group of functionalized surfactants can affect their properties, (ii) the most prominent effects are observed in dimeric surfactants and (iii) the replacement of imidazolium ring by tetraalkylammonium fragment gives rise to a decrease in the micellar effects. Therefore, functionalized dimeric imidazolium surfactants are more appropriate for use in designing new supernucleophilic systems.

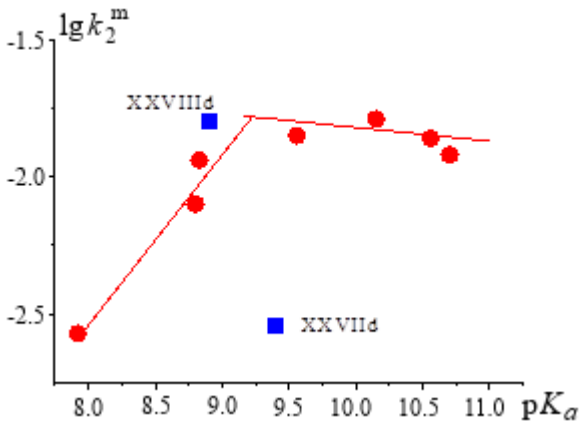


Fig. 22. Brønsted plots for decomposition of NPOTos by oxime-functionalized surfactants XXVIId and XXVIIId, the remaining (open circles) were taken from [52, 54].

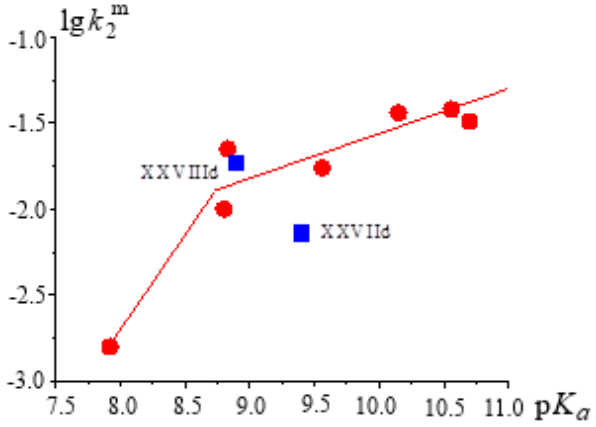


Fig. 23. Brønsted plots for decomposition of NPDEP by oxime-functionalized surfactants XXVIId and XXVIIId, the remaining (open circles) were taken from [52; 54].

CONLUSIONS

The present study is aimed at establishing the regularities in self-organization and relationships «chemical structure – supramolecular architecture – functional activity of nano-sized systems», and designing new micro- and nano-containers and reactors with controllable properties.

Of special interest as host molecules are dimeric (Gemini) surfactants capable of forming a variety of micelles in aqueous solutions. The main advantage of Gemini surfactants is that they exhibit the properties which result in increased efficiency of the systems on their basis. The use of Gemini for esterolytic reactions poses a number of fundamental problems. Whether the regularities in decomposition of esters in micelles of cationic Gemini and those of monomeric surfactants involving nucleophiles under study are general? How wide is the kinetic range for some of these reaction in the micellar medium involving Gemini? How much changes in the spacer length affect the reaction rates of such reactions?

The present study dealt with OMS based on cationic dimeric and functionalized surfactants as well as those with a reactive counterion, in decomposition of compounds similar in structure and behavior of ecotoxic substrates.

Detailed studies on physico-chemical characteristics and kinetic behavior of various surfactants in decomposition of acyl substrates, including toxic organophosphorus compounds, make it possible to evaluate the role of structure factors in micellar effects of surfactants and formulate the ways to modifications of OMS.

Micellar effects in the surfactants under study depend on the structural features of both the surfactant and substrate. The esters under study are electrically neutral compounds, i.e. the main driving force of substrate binding is hydrophobic interactions, which, in turn, depend on hydrophobic properties of surfactant. An increase in the length of alkyl “tail” is accompanied by an increase in the observed rate constant of alkaline hydrolysis both of BrO^- ion and oximate group. In this case

the effect of the length of alkyl substituent does not change in comparison with that in monomeric counterpart. In addition, micelles of dicationic Gemini surfactants provide better surrounding for nucleophilic deacylation compared with corresponding monocationic micelles. Such kinetic advantages of Gemini surfactants can be caused by the spacer chain resulting in decreased water penetration at the micellar surface. Dephosphorylation and deacylation reactions proceed, in general, easier under decreased water content of reaction surrounding and, in turn, depend on the nature of spacer.

There is no doubt that the substrate hydrophobicity and change in reactivity in transferring the decomposition process into micellar pseudophase contribute also to the efficiency of micellar catalysis. In most cases the observed reaction rates of NPDEPN are higher, whereas those for NPOTos and NPDEP are comparable in magnitude. However, in all cases micellar effects are governed by reagent concentrating in the Stern layer, microenvironment polarity changes, and depend on the ratio of their contributions to the observed reaction rates.

It should be particularly emphasized that in micelles of Gemini the observed reaction rates at every concentration used are an order of magnitude (or even more) higher compared with those in micelles of monomeric surfactants. Therefore, the systems for decomposition of ecotoxicants involving Gemini surfactants will be more acceptable environmentally. However, there is another obstacle to the application of dimeric surfactants. Maximum increase in reaction rates was detected for OMS at Alk = $C_{16}H_{33}$, but there are certain difficulties associated with the solubility of surfactant themselves. This issue can be partially resolved by adding co-surfactant, such as CTAB. In this case an increase in solubility is accompanied by a decrease in micellar effects, so the selection of suitable experimental conditions «micellar composition – micellar effects» are of prime consideration.

In closing: whether kinetic efficiency of such reactions can be enhanced by suitable modification of the host surfactant, or any other skeleton is necessary? The follow-on studies are now in progress.

CONFLICT OF INTERESTS;
The authors declare no conflict of interests

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