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Functional Detergents Containing an Imidazole Ring and Typical Fragments of α-Nucleophiles Underlying Micellar Systems for Cleavage of Esters of Prosphorus Acids

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Abstract—1-Cetyl-3-(2-oximinopropyl)imidazolium, 1-cetyl-3-(2-oxaminoethyl-2-one)imidazolium, and 1-cetyl-3-(2-amino-2-oximinoethyl)imidazolium halides were synthesized. These compounds form in water solutions functional zwitter-ionic micelles as surfactants. The cleavage kinetics of 4-nitrophenyl diethyl phosphate, 4-nitrophenyl ethyl ethylphosphonate, and 4-nitrophenyl tosylate in micelles of the functional detergents and combined micelles of the functional detergents with cetyltrimethylammonium chloride are adequately described in a framework of a simple pseudophase distribution model, and the micellar systems of the detergents are typical α-nucleophilic reagents. An equation was suggested for quantitative estimation of the micellar effect of the surfactants that took into account the change in the nucleophilic and basic characteristics of the α-nucleophilic center of the detergent and also the influence of the reagents concentrating on transition of the reaction from the water into micelle phase. The maximum acceleration of the S_N2-reaction in the micelles of the functional zwitter-ionic detergents for the cleavage of 4-nitrophenyl diethyl phosphate and 4-nitrophenyl tosylate reached 3500 and 75 000 (oximate surfactant), 3300 and 66 000 (amidoximate surfactant), and 4800 and 12200 (hydroxamate surfactant) times respectively. New functional detergents underlie unique supernucleophilic micellar system affording extremely high cleavage rates of organophosphorus substrates-ecotoxicants.

Organophosphorus compounds (paraoxone **I**, armin **II**, GD, and VX) comprise a group of especially dangerous ecotoxicants-neurotoxins [1], and the most toxic among them, GD and VX, are constituents of chemical warfare agents. Organophosphorus compounds and chemical warfare agents relatively fast react with α-nucleophiles [1–8], and the typical representatives of the latter: 1-methyl-2-oximinomethylpyridinium iodide, dipiroxime, toxogenin [1], halides of 1-methyl-3-(2-oximinopropyl)-imidazolium [9, 10] etc. [7–8] are efficient reactivators of choline esterase inhibited by the organophosphorus compounds. However the rate of decontamination from the organophosphorus compounds depends not only on the reactivity of the α-nucleophiles but also on the dissolution rate of organophosphorus compounds in the solvent used, and therefore it frequently gives a paradoxical result: although the given α-nucleophile possesses high reactivity, the decontamination rate is low [11].*

Therefore these two events were always taken in consideration in formulating the solvent systems capable to ensure fast and irreversible cleavage of organophosphorus compounds and chemical warfare agents [12–14]. We formerly demonstrated [14–16] by an example of cleavage of substrates **I** and **II**, and 4-nitrophenyl tosylate **III** with 1-cetyl-3-(2-oximinopropyl)imidazolium halides that the micelles of the surfactant to a certain extent removed the problem of ecotoxicants solubilization, and the process rate was controlled only by con-

* Decontamination of a chemical warfare agent with water-organic formulation is a multistage process where the first stage consists in dissolution of a drop of the warfare agent in the volume of decontaminating solution, and then in the following stages occurs its chemical cleavage.

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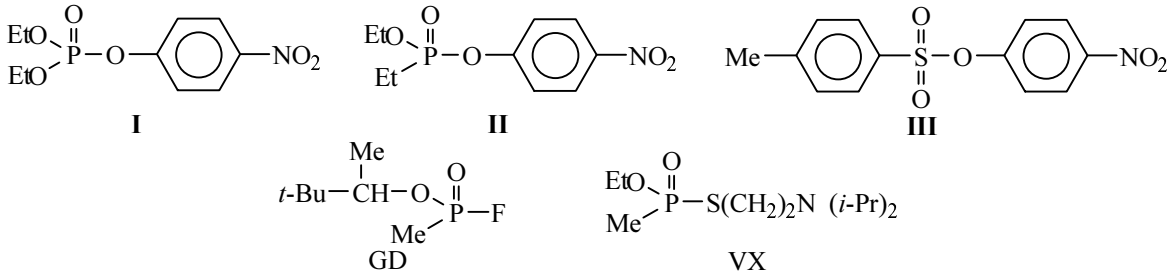
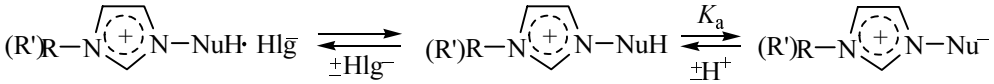


I **II** **III**

GD VX

The goal of the present study was investigation of O-nucleophilic properties and solubilizing qualities in the micelles of detergents we had synthesized for the first time that contained in their head group an imidazolium ring with α-nucleophile groups covalently linked thereto (halides of 1-cetyl-3-(2-oximinopropyl)imidazolium **IV**, 1-cetyl-3-(2-amino-2-oximinoethyl)imidazolium **VI**, 1-cetyl-3-(2-oxaminoethyl-2-one)imidazolium **VIII**, and of their methyl analogs **V**, **VII**, and **IX**, equation 1) and in combined micelles of functional and cationic detergent (cetyltrimethyammonium chloride, CTAC). As substrates for cleavage reaction stady were selected 4-nitrophenyl diethyl phosphate (paraoxone **I**), 4-nitrophenyl ethyl ethylphosphonate (armin **II**), and 4-nitrophenyl tosylate **III**. The first two substrates are extremely toxic compounds modeling the chemical warfare agents ($LD_{50} \le 1.0$ mg/kg) [1, 5]. We choose the substrate **III** for its pronounced hydrophobic properties that provided a possibility to estimate and understand the role of hydrophoby in binding of the substrate by the micelles of the functional detergents. The characteristic feature of the functional detergents under study consists in variation of the surfactant structure only by changing the nature of the α-nucleophilic moiety in the head part of the molecule. It was possible therefore to compare the nucleophilic properties of the functional detergents and their methyl analogs in water and micellar medium. No less important is the elucidation of factors governing the micellar effects of the functional surfactants.



(R')RIm$^+$NuH (R')RIm$^+$Nū (1)

IV–IX **IVa–IXa**

NuH = $-CH_2-C(CH_3)=N-OH$, R = $C_{16}H_{33}$ (IV), R' = CH_3 (**V**) **IVa, Va**

NuH = $-CH_2-C(NH_2)=N-OH$, R = $C_{16}H_{33}$ (VI), R' = CH_3 (**VII**) **VIa, VIIa**

NuH = $-CH_2-C(=O)-NH_2$ OH, R = $C_{16}H_{33}$ (**VIII**), R' = CH_3 (**IX**) **VIIIa, IXa**

$Hlg^- = Cl^-, Br^-$

In water the oximate, amidoximate, and hydroxamate anions **IVa–IXa** generated from bromides **IV–IX** (reaction 1) as typical α-nucleophiles rapidly react with substrates **I–III** [6–11, 14–17]. The reaction of zwitter-ions **IVa–IXa** with these esters (equation 2) involves a nucleophilic attack on the electrophylic site of the substrate by the zwitter-ion form $R'Im^+Nu^-$, RIm^+Nu^- and affords the corresponding O-acyl derivatives of the α-nucleophiles [18].

$$(R)R'Im^{+}Nu^{-} + Acyl-O-PhNO_2 \longrightarrow AcylNuIm^{+}R'(R) + {}^{-}O-PhNO_2 \quad (2)$$

Acyl = $(EtO)_2P{=}O$, $Et(EtO)P{=}O$, Ts.

The dependence of the apparent rate constants of pseudofirst order k_{app}, s^{-1} on the analytical concentration of salt $[R'Im^{+}NuHHlg^{-}]_0$, mol l^{-1}, is typical for processes involving as the reactive form the main component of the buffer, $R'Im^{+}Nu^{-}$, and the reaction itself is not complicated by associative interactions. The reaction rate grows both with increasing pH (pH-profile, see Fig. 1a) and zwitterion concentration (concentration profile, see Fig. 1b) and is described by an expression:

$$k_n = k_2^W [R'Im^{+}Nu^{-}] = k_2^W \alpha_{R'Im^{+}Nu^{-}} [R'Im^{+}NuH]_0, \quad (3)$$

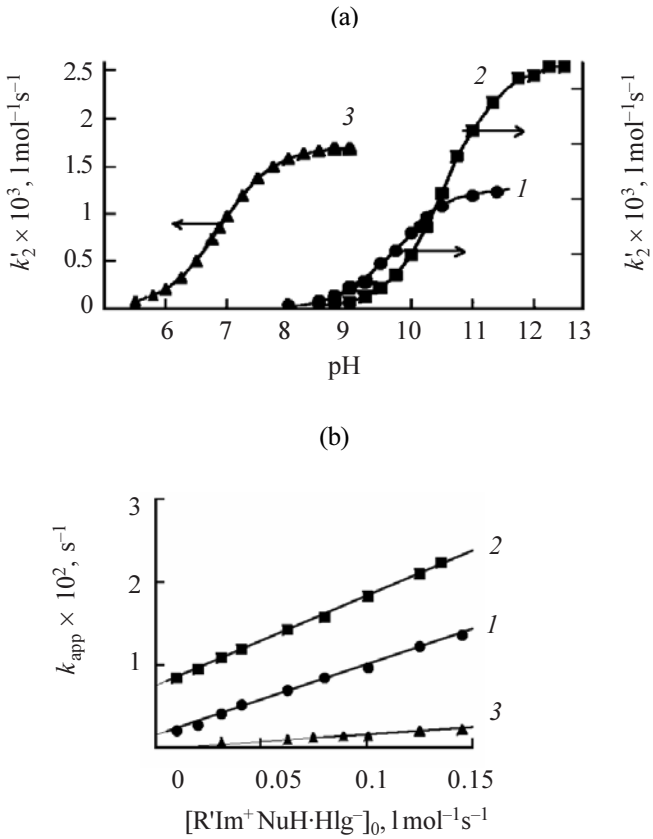


Fig. 1. Dependence of cleavage rate of 4-nitrophenyl diethyl phosphate **I** and 4-nitrophenyl ethyl ethylphosphonate **II** on pH of the medium and on the analytical concentration of the α-nucleophile; water, 25°C, m = 1.0 (KCl). (a) pH-profiles for reactions of 1-methyl-3-(2-oximinopropyl)imidazolium **V** (*1*), 1-methyl-3-(2-amino-2-oximinoethyl)imidazolium **VII** (*2*), 1-methyl-3-(2-oxaminoethyl-2-one)imidazolium **IX** (*3*) with 4-nitrophenyl diethyl phosphate **I**; $k_2' = k_{app}/[R'Im^{+}NuHHlg^{-}]_0$, l mol^{-1} s^{-1}; (b) concentration profiles for reactions of 1-methyl-3-(2-oximinopropyl)imidazolium **V** (*1*, pH 12.0), 1-methyl-3-(2-amino-2-oximinoethyl)imidazolium **VII** (*2*, pH 12.7), and 1-methyl-3-(2-oxaminoethyl-2-one)imidazolium **IX** (*3*, pH 10.0) with 4-nitrophenyl ethyl ethylphosphonate **II**.

where $a_{R'Im^{+}Nu^{-}} = K_a/(K_a + a_{H^{+}})$ is the fraction of zwitterion form of the a-nucleophile, and K_a is the ionization constant of its conjugate acid. The second rate constants k_2^s, l mol^{-1}s^{-1}, characterizing the nucleophilic property of the zwitter-ions $R'Im^{+}Nu^{-}$ were calculated by equation (3), and their values are presented in Table 1. Zwitter-ions **Va**, **VIIa**, and **IXa** do not show any abnormal kinetic behavior, and their reactivity fits to the corresponding Bronsted dependences for esters **I–III** [6].

Functional detergents **IVa**, **VIa**, and **VIIIa** unlike their methyl analogs **Va**, **VIIa**, and **IXa** affect the rate of esters cleavage in a specific fashion. Up till the critical concentration of micelles formation (CCMF) the reaction rate grows a little as compared with the methyl analogs of the detergents. In this range only alkaline hydrolysis of substrates **I–III** is observed. With the growth of concentration of the detergent after micelles formation ($C = C_0$ – CCMF, mol l^{-1}) the rate of ester cleavage (k_{app}, s^{-1}) significantly increases because of the substrate transfer into the zwitter-ionic micelles of the surfactant (Figs. 2a, 2b). At the total binding of the substrate in the micelles of detergent **IVa** the cleavage rate becomes independent of the analytical concentration of the surfactant, $k_{app} \rightarrow k_{app\ max.} = k_m$, and the S_N2-reaction (equation 2) occurs in the micellar pseudophase.*

Similar kinetic relations were observed in the cleavage of ester **II** by the combined system micellar **IVa**/CTAC and in reactions of combined micellar systems of variable **IVa**/CTAC, **VIa**/CTAC, and **VIIIa**/CTAC with substrates **I** and **III**. Concentration profiles obtained at pH of the medium ensuring the complete ionization of the α-nucleophilic fragments of the surfactant in the combined micelle show that after reaching the critical concentration of micelles formation the reaction rate grows quickly and attains a plateau level with the maximum value of $k_{app} = k_m'$ at the given ω value (ω is a molar fraction of the zwitter-ionic detergent in the combined micelle $RIm^{+}Nu^{-}$/CTAC, Fig. 3). After correcting k_{app}' value for the contribution of the alkaline hydrolysis that usually did not exceed 5%, from the relation of k_m' to the molar fraction of the zwitter-ionic surfactant (equation 4) the values of k_m were calculated (Table 1).

* In view of limited solubility of the zwitter-ionic forms of detergents **VIa** and **VIIIa** the initial concentrations of surfactants **VI** and **VIII** were varied in the range 2×10^{-5}–3×10^{-3} mol l^{-1}

$$k'_m = k_m\omega = k_2^m[RIm^+Nu^-]_m \quad (4)$$

The established relations of type (4) correspond to the concentration character of the effect of the functional surfactants on the rate of ester cleavage. At infinite dilution of the detergent when ω>0 the rate of the process k'_m>0, and at ω>1, k_m>k_m, i.e. corresponds to the rate of reaction of **IVa**, **VIa** or **VIIIa** with substrate in the micelles of the functional surfactants. The variation in the composition of the combined micelles did not change the nucleophilicity of zwitter-ionic detergents **IVa**, **VIa**, and **VIIIa**, and the decrease in the k'_m values originates from the "dilution" of the micellar pseudophase with the cationic detergent CTAC and from the reduction of the "local" concentration of RIm^+Nu^--form in the combined micelle (Fig. 4). This assumption is confirmed by coincidence of k'_m values for detergents **IVa**, VIa, and **VIIIa** calculated from expression (4) and obtained from independent experiments (Table 1).

Functional detergents **IV, VI**, and **VIII** fall in the class of weak acids , and therefore the composition of the combined micelles RIm^+Nu^-/CTAC depends on pH of the medium.

At complete binding of the substrate by the combined micelles RIm^+Nu^-/CTAC the pH-profiles of the reaction (Fig. 5) are described by equation (5):

$$K_{app} = k_2^m [RIm^+Nu^-]_m = k_m \omega \alpha_{RIm^+Nu^-}, \quad (5)$$

where $[RIm^+Nu^-]_m$ is the "local"concentration of the zwitter-ionic detergent in the micellar phase; $a_{RIm^+Nu^-} = K_{a,app.}/(K_{a,app} + a_{H^+})$ is the fraction of the zwitter-ionic form of the detergent RIm^+NuH; $K_{a,app}$ is its apparent acid ionization constant at w = const; k_2^m, l mol^{-1} s^{-1}, is the second order rate constant characterizing the nucleophilicity of the RIm^+Nu^--forms of the detergents in micellea and combined micelles of surfactants. Transforming the latter expression into (6) we found from relations "$k_{app} - k_{app}\, a_{H^+}$" (Fig. 6) the corresponding values of k'_m and $K_{a,app}$ for all functional detergents (Tables1 and 2).

$$K_{app} = k'_m - (k_{app}/K_{a,app})a_{H^+} \quad (6)$$

Two important points command the attention. Firstly, the k_m values coincide with those calculated from expression (4) evidencing the validity of approaches used for their evaluation. Secondly, CTAC considerably affects the acid ionization constants of detergents **IV**, **VI**, and

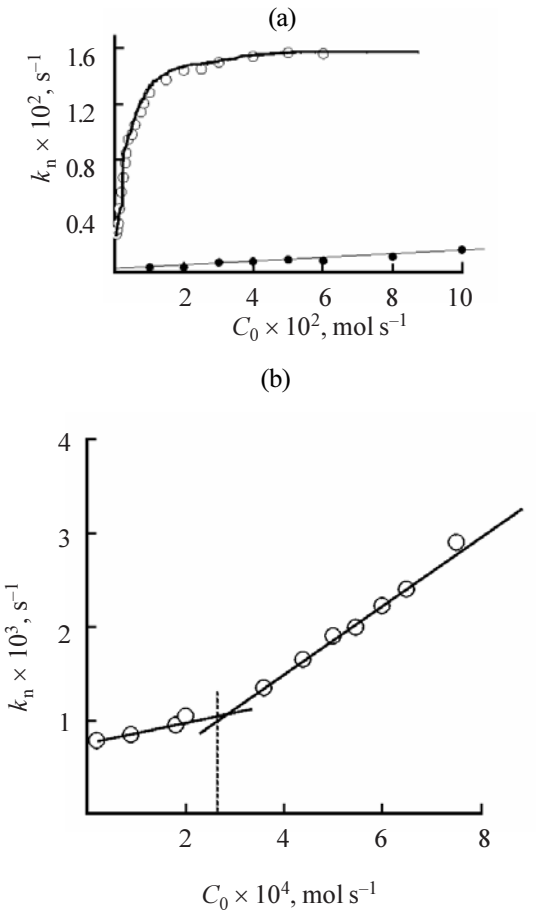


Fig. 2. Concentration profiles for the cleavage of 4-nitrophenyl diethyl phosphate I with functional detergents and their methyl analogs. (a) Reaction of 4-nitrophenyl diиethyl phosphate **I** with 1-cetyl-3-(2-oximinopropyl)imidazolium **IVa** (1) and 1-methyl-3-(2-oximinopropyl)imidazolium **Va** (2); pH 12.9; (b) initial part of the concentration profile for the cleavage of 4-nitrophenyl diethyl phosphate I with 1-cetyl-3-(2-oximino-propyl)imidazolium **IVa** (1); pH 12.9.

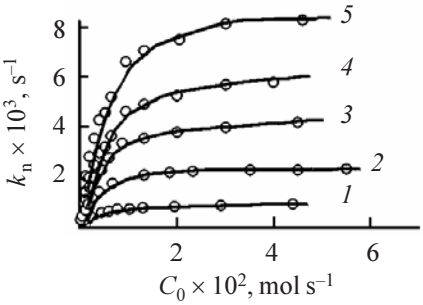


Fig. 3. Concentration profiles for the cleavage of 4-nitrophenyl diethyl phosphate **I** in combined micelles **IVa**/CTAC at complete ionization of the α-nucleophilic fragment of the detergent. (*1*) ω = 0.714, pH 12.60; (*2*) ω = 0.5, pH 12.50; (*3*) ω = 0.333, pH 12.40; (*4*) ω = 0.167, pH 12.00; (*5*) ω = 0.091, pH 11.60.

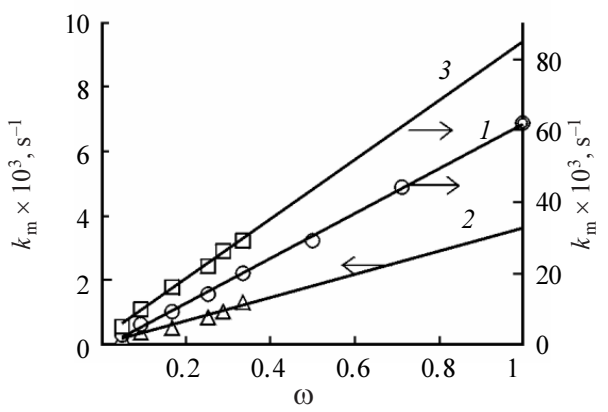


Fig. 4. Effect of the composition of combined micelle RIm^+Nu^-/CTAC on the rate of cleavage of 4-nitrophenyl- tosylate **III**; (*1*) (**IVa**)/CTAC), (*2*) (**VIa**)/CTAC, (*3*) (**VIIIa**)/CTAC).

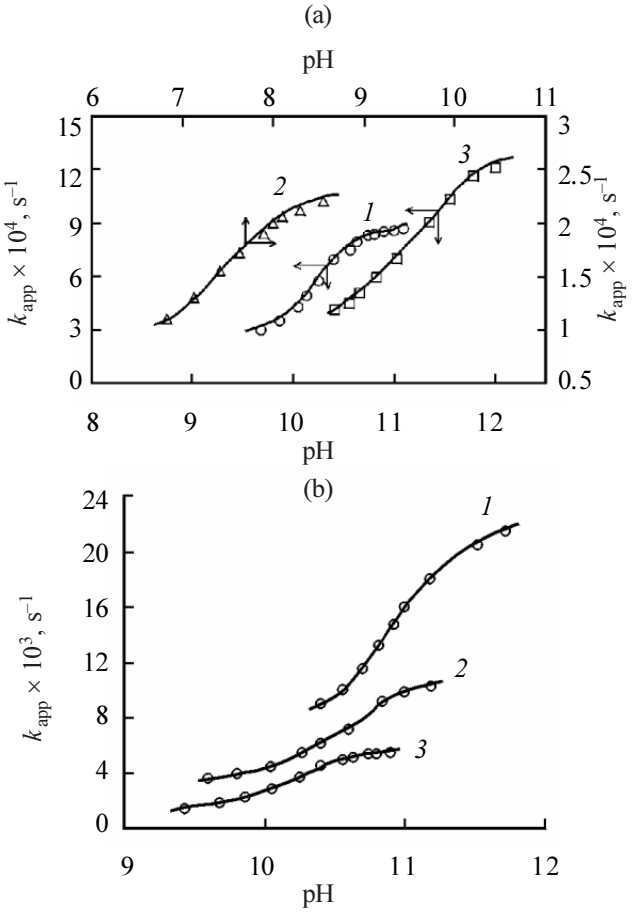


Fig. 5. pH-Profiles for the cleavage of 4-nitrophenyl diethyl phosphate **I** and 4-nitrophenyl tosylate **III** by combined micelles RIm^+Nu^-/CTAC. (a) Reaction of 4-nitrophenyl diethyl phosphate **I** with combined micelles **IV**/CTAC (*1*, $C_0 = 4.4 \times 10^{-3}$ mol l^{-1}), **VI**/CTAC (*2*, $C_0 = 8.8 \times 10^{-3}$ mol l^{-1}) and **VIII**/CTAC (*4*, $C_0 = 9.9 \times 10^{-3}$ mol l^{-1}) at ω = 0.091;(b) reaction of 4-nitro-phenyl tosylate **III** with combined micelles **IV**/CTAC at ω = 0.5 (*1*), ω = 0.118 (*2*) and ω = 0.091 (*3*); $C_0 = 1.5 \times 10^{-2}$ mol l^{-1}.

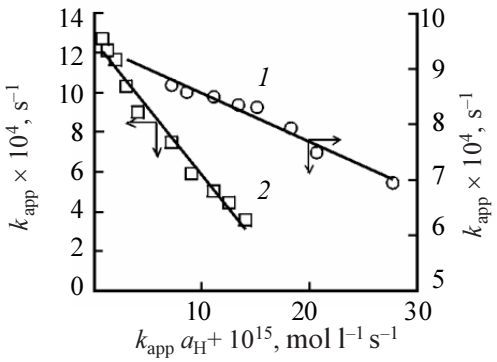


Fig. 6. Apparent rate constants k_{app}, s^{-1} as a function of values $k_{app}\, a_{H^+}$, l mol^{-1} s^{-1}, for the cleavage of 4-nitrophenyl diethyl phosphate **I** in combined micelles **IVa**/CTAC (*1*) and **VIa**/CTAC (*2*) at ω = 0.091.

VIII, and the character of its effect on the $pK_{a,app}$ values is expressed by relations (7–9):

$$pK_{a,app}(\mathbf{IV}) = (9.95 \pm 0.05) + (1.70 \pm 0.10)\,\omega,\ r = 0.985,\ n = 7 \quad (7)$$

$$pK_{a,app}(\mathbf{VI}) = (10.80 \pm 0.02) + (1.85 \pm 0.10)\,\omega,\ r = 0.992,\ n = 5 \quad (8)$$

$$pK_{a,app}(\mathbf{VIII}) = (7.04 \pm 0.02) + (1.40 \pm 0.08)\,\omega,\ r = 0.985,\ n = 5 \quad (9)$$

Angular coefficients of dependences (7–9) (Fig. 7) correspond to the maximum change in the $pK_{a,app}$ value on transition of detergent RIm^+NuH from a cationic ($w \to 0$) into a zwitter-ionic micelle ($w \to 1$) of the surfac-

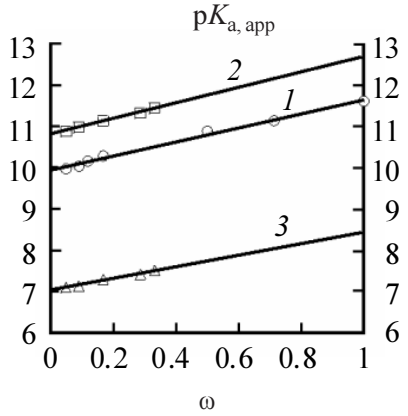


Fig. 7. Dependence of $pK_{a,app}$ values for 1-cetyl-3-(2-oximinopropyl)imidazolium **IV** (*1*), 1-cetyl-3-(2-amino-2-oximino-ethyl)imidazolium **VI** (*2*), and 1-cetyl-3-(2-oxaminoethyl-2-one)imidazolium **VIII** (*3*) on molar fraction of functional detergent (ω) in combined micelles **IVa**/CTAC, **VIa**/CTAC, and **VIIIa**/CTAC.

Table 1. Rate constants[a] k'_m, s^{-1}, for cleavage of 4-nitrophenyl diethyl phosphate **I**, 4-nitrophenyl ethyl ethylphosphonate **II**, and 4-nitrophenyl tosylate **III** in micellar phase of functional detergent/CTAC, nucleophilicity constants k_2^s, l mol^{-1} s^{-1}, 1-cetyl-3-(2-oximinopropyl)-imidazolium **IVa**, 1-cetyl-3-(2-amino-2-oximinoethyl)imidazolium **VIa**, 1-cetyl-3-(2-oxaminoethyl-2-one)imidazolium **VIIIa**, and constants of substrate binding K_S, l mol^{-1}; water, 25 °C

ω[b]	IVa			VIa			VIIIa			V_m[d]
	$k'_m \times 10^3$	$k_2^s \times 10^3$	K_S (P_S)[c]	$k'_m \times 10^3$	$k_2^s \times 10^3$	K_S (P_S)[c]	$k'_m \times 10^3$	$k_2^s \times 10^3$	K_S (P_S)[c]	
4-nitropheny diethyl phosphate **I**										
1	16[e] 16.3[c]	88.25	280 (560)	20.3[e]	10.15 10.0[g]	280 (560)270 (540)	3.8[e]	1.9 2.2[g]	280 (560)290 (580)	0.500.50
0.714	11.0	7.06	270 (590)		–	–	–	–	–	0.46
0.5	7.9	6.79	280 (650)	–	–	–	–	–	–	0.43
0.333	4.6	5.65	300 (730)	7.6	9.33	290 (710)	1.3	1.60	270 (660)	0.41
0.286	–	–	–	6.0	8.46	300 (740)	1.0	1.41	340 (840)	0.40
0.25	3.9	6.22	300 (750)	–	–	–	1.0	1.60	300 (750)	0.40
0.167	2.5	5.82	380 (980)	3.2	7.45	320 (820)	0.62	1.44	280 (720)	0.39
0.118	1.85	6.06	360 (940)	2.4	7.86	310 (810)	0.48	1.57	280 (730)	0.38
0.091	1.45	6.06	380 (1000)	1.8	7.52	320 (840)	0.35	1.46	290 (760)	0.38
0.048	0.75	5.87	300 (800)	1.0	7.82	320 (850)	0.16	1.25	310 (830)	0.38
–		8.40[h]			17[h]			1.70[h]		
4-nitrophenyl ethyl ethylphosphonate **II**										
1	320[e] 300[f]	160150	260 (520)	360	180[g]	280 (580)	36	18[g]	260 (520)	0.500.50
0.5	152	130	280(560)	–	–	–	–	–	–	0.43
0.167	52	121	280 (560)	–	–	–	–	–	–	0.39
0.091	28	120	270 (540)	–	–	–	–	–	–	0.38
–	–	90[h]	–	–	100[h]	–	–	14[h]	–	–
4-nitrophenyl tosylate **III**										
1	62[e] 62.5[f]	31.230	3300 (6600)	83[e]	41 38[g]	3200 (6400)3100 (6200)	3.65[e]	1.80 1.5[g]	3300 (6600)3100 (6200)	0.500.50
0.714	44	28.2	3400 (7400)	–	–	–	–	–	–	0.46
0.5	29	25	3400 (7900)	–	–	–	–	–	–	0.43
0.333	20	24.6	3300 (8050)	29	35.7	3500 (8500)	1.3	1.6	3600 (8800)	0.41
0.286	–	–	–	26	36.6	3500 (8700)	1.0	1.4	3400 (8400)	0.40
0.25	14	22.4	3200 (8000)	22	35.2	3300 (8250)	0.85	1.36	3300 (8250)	0.40
0.167	9	21	3200 (8200)	16	37.3	3400 (8700)	0.52	1.23	3100 (8000)	0.39
0.091	5.6	23.4	3200 (8400)	9.9	41.3	3300 (8700)	0.36	1.5	3200 (8400)	0.38
0.048	2.8	21.9	3100 (8250)	5	39	3200 (8500)	0.2	1.56	3100 (8250)	0.38
		15.0[h]			48[h]			4.10[h]		

[a] Errors in determination of k'_m, k_2^s, and K_S values do not exceed ±10%.
[b] ω is the molar fraction of the functional detergent in combined micelle functional detergent/CTAC.
[c] Substrate distribution factor $P_S = K_S/V_m$.
[d] V_m, l mol^{-1}, calculated by equation (15).
[e] Determined at ω = 1 [14, 15].
[f] Calculated by equation (4).
[g] Estimated by equation (13).
[h] Values of k_2^s for methyl analogs **Va**, **VIIa**, and **IXa**; m = 1,0 (KCl).

Table 2. Effect of CTAC on apparent acid ionization constants ($pK_{a,app}$) of 1-cetyl-3-(2-oximinopropyl)imid-azolium **IV**, 1-cetyl-3-(2-amino-2-oximinoethyl)imidazolium **VI**, and 1-cetyl-3-(2-oxaminoethyl-2-one)imidazolium **VIII**; water, 25 °C

Molar fraction of functional surfactant in combined micelle, ω	$pK_{a,app}$		
	IVa	**VIa**	**VIIIa**
1	11.60 11.65[a]	12.65 [a]	8.44[a]
0.714	11.15	–	–
0.5	10.93	–	–
0.333	–	11.42	7.50
0.286	–	11.33	7.43
0.167	10.32	11.18	7.30
0.118	10.21	–	–
0.091	10.04	10.95	7.15
0.048	9.96	10.90	7.10
ω→0	9.94[a]	10.80[a]	7.04[a]
H_2O[b]	10.67	11.70	7.88

[a] Calculated from equations (7–9).
[b] Basicity of zwitter-ionic forms of methyl analogs **Va**, **VIIa**, and **IXa** in water.

tant. Thus at w→0 the $pK_{a,app}$ value corresponds to the acidity of a specific fragments of the functional RIm^+NuH at indefinitely small concentration in micelles of CTAC, and at ω→1 it is equal to the acidity of an a-nucleophilic fragment of the RIm^+NuH molecule in zwitter-ionic micelles of **IVa**, **VIa**, and **VIIIa**. This effect of the cationic detergent CTAC on the acid-base properties of detergents **IV**, **VI**, and **VIII** is an uncommon phenomenon that we first discovered. Usually the pK_a values of weak neutral acids are reduced at their solubilization by surfactant micelles. This is understood from the viewpoint of the difference between distribution factors of a base and its conjugate acid, that is, as an effect of prevailing concentrating anionic forms compared to neutral ones [19]. This rationalization of the phenomenon is hardly exhaustive in the case of functional detergents **IV**, **VI**, and **VIII** since the detergent is a component of the arising combined micelle. The scope of the experimental data obtained in this study is insufficient for interpretation of the phenomenon observed, and the character of the change in pK_a should be investigated in micelles of various surfactants: neutral, anionic, cationic, and zwitter-ionic.

Quantitative description of the behavior of the functional detergents and their systems of combined micelles in reactions of cleavage of esters **I–III** requires not only the data on kinetic parameters, k_m, s^{-1}, values, but also thermodynamical information, values P_S characterizing the substrates (S) distribution between water (S_w) and micellar (S_m) phases (equation 10).

$$P_S = ([S]_m)/([S]_w) = K_S/V_m - 1 \quad (10)$$

In this equation V_m, $l\ mol^{-1}$, is the partial molar volume of the region in the micelles or combined micelles of the surfactants where the substrate is located and the S_N2-reaction occurs, and K_S, $l\ mol^{-1}$, is the binding constant describing the efficiency of substrate solubilization with the micellar system [19]. The cleavage of esters **I–III** promoted in micelles is described by the scheme of reaction (11). It proceeds along two parallel routes and includes alkaline hydrolysis of the ester in water ($k^w_{app,OH} = k^w_{OH}[OH^-]_w$, s^{-1}) and the reaction of RIm^+Nu^- with the substrate in the micellar phase ($k'_m = k^m_2[RIm^+Nu^-]$, s^{-1}).

$$\begin{array}{ccc} (S)_m & \xrightarrow{k^m_2[RIm^+Nu^-]_m} & \text{Reaction products} \\ P_S \uparrow\downarrow & & \\ (S)_w & \xrightarrow{k^w_{OH}[OH^-]_w} & \text{Reaction products} \end{array} \quad (11)$$

The contribution of the alkaline hydrolysis into the measured k_{app} values is usually small, and as follows from expression (12) it quickly decreases with growing C. However it is necessary for to take into account alkaline media at $K_SC \ll 1$.

$$k_m = \frac{k^m_2[RIm^+Nu^-]_m\ K_S\ C}{1 + K_S\ C} + \frac{k^w_{OH}\ [OH^-]_w}{1 + K_S\ C} \quad (12)$$

$$k_m = k'_m - \frac{k_m - k^w_{OH}\ [OH^-]_w}{K_S\ C} \quad (13)$$

Applying the approach we had developed formerly [16] and taking into account the contribution of the alkaline hydrolysis with the use of expression (13) we calculated K_S values for the systems of individual and combined micelles under study.

$$k^m_2 = k'_m \frac{1}{\omega}\ V_m \quad (14)$$

The values of $k'_m = k_m\omega$ and K_S compiled in Table 1 are effective kinetic and thermodynamic parameters. The determination of the second order rate constant k^m_2 (equation 14) and distribution factor P_S (equation 10) requires the knowledge of the partial molar volume V_m for micelle RIm^+Nu^- and combined micelle RIm^+Nu^-/CTAC.

For S_N2-reactions of anionic nucleophiles with electroneutral substrates accelerated with micelles of cationic surfactants and with combined micellar systems the k_2^m values are of the same order of magnitude or a little smaller than the second order rate constants for these nucleophiles in water [20–24]. These differences as also difference values of P_S, are often due to the choice of V_m values. For trimethylammonium micelles this value is usually believed to lie in the range V_m^+=0.14–0.37 l mol^{-1} [20]. Zwitter-ionic detergents **IVa**, **VIa**, and **VIIIa** contain bulky head groups (equation 1), and this is one of the principal factors governing V_m. Therefore we chose for RIm$^+$Nu$^-$ a value $V_m^\pm$ = 0.5 l mol^{-1}, since just this value was used in description of nucleophilic reactions in metallomicelles where the volume of the head groups is relatively big [21] and apparently close to that of detergents **IVa**, **VIa**, and **VIIIa**. In evaluation of k_2^m and P_S values for reactions in cationic micelles of CTAC the value of V_m^+ = 0.37 l mol^{-1} was taken whereas for systems with combined micelles **IVa**/CTAC, **VIa**/CTAC, and **VIIIa**/CTAC the partial molar volume was calculated by additive scheme along expression (15).

$$V_m = \frac{V_m^+ d^+(1-\omega) + V_m^\pm d^\pm \omega}{d^+(1-\omega) + d^\pm \omega}, \quad (15)$$

where V_m^+, $V_m^\pm$ are partial molar volumes of cationic and zwitter-ionic detergent respectively in micellar form, and d^+ and $d^\pm$, g ml^{-1}, are their densities.* The corresponding values of k_2^m, K_S, P_S, and V_m calculated from expressions (5), (12), (14), and (15) are listed in Table 1.

Interestingly, the kinetic and thermodynamic reaction parameters, k_2^m and P_S, do not suffer significant changes at variation of the composition of the micellar pseudophase. Inasmuch as k_2^m and P_S describe the reactivity of the functional detergent and the solubilizing efficiency of the micelle it may be considered that the physicochemical characteristics are constant in the regions of the micellar medium where the substrate is located and where esters **I–III** are cleaved by zwitter-ionic detergents **IVa**, **VIa**, and **VIIIa**. At the same time the transfer of the reaction from water phase into the pseudomicellar phase of individual and combined micelles does not lead to changes in the reactivity of α-nucleophilic centers, and they form the same nucleophilicity sequence as their methyl analogs: micellar phase, **VIa** > **IVa** > **VIIIa**; water pseudophase, **VIIa** > **Va** > **IXa** as follows from comparison of k_2^m and k_2^w values presented in Table 1.

$$k_m = \frac{k_2^m[\mathrm{RIm^+Nu^-}]_m K_S C}{1 + K_S C} = \frac{k_m' K_S C}{1 + K_S C} \frac{K_{a,app}}{K_{a,app} + a_{H^+}} \quad (16)$$

The analysis of kinetic behavior of zwitter-ionic detergents RIm$^+$Nu$^-$ performed in the framework of a simple pseudophase distribution model evidences that the consumption of esters **I–III** in the individual and combined micelles of surfactants fits to the rate law (16) that is valid within a wide range of pH ($K_{a,app} \ll a_{H^+} \ll K_{app}$) and concentrations C ($1 \ll K_S C \ll 1$).

The kinetic relations calculated by equation (16) for various experimental conditions and represented by solid lines on Figs. 2, 3, and 5 excellently describe the pH- and concentration profiles of reactions involving detergents **IVa**, **VIa**, and **VIIIa** once more testifying to the validity of equation (11).

The quantitative evaluation of the micellar effects of the zwitter-ionic detergents RIm$^+$Nu$^-$ provides a possibility to elucidate what factors control the rate of esters **I–III** cleavage and what driving force promotes the transfer of the reaction from water into the phase of individual and combined micelles of the surfactant. This problems we solve with the use of expression (17) where the value $\Delta = \Delta_1\Delta_2\Delta_3$ is given as the ratio of the reaction rate of the detergent RIm$^+$Nu$^-$ in the micellar phase [k_{app}(RIm$^+$Nu$^-$)] to the reaction rate of its methyl analog in water [k_{app}(R'Im$^+$Nu$^-$)] at [R'Im$^+$Nu$^-$]$_0$ = ωC. We assume that the second order rate constants for nucleophiles RIm$^+$Nu$^-$ and R'Im$^+$Nu$^-$ in water are close in values since their basicity is similarly affected by the inductive effect of the methyl and cetyl groups.

$$\Delta = \Delta 1 \cdot \Delta 2 \cdot \Delta 3 = \frac{k_n[\mathrm{RIm^+Nu^-}]}{k_n[\mathrm{R'Im^+Nu^-}]}$$

$$= \frac{k_2^m}{k_2^w} \frac{P_S C \omega}{[\mathrm{R'Im^+NuH}]_0(1 + K_S C)} \frac{K_{a,app}(K_a + a_H^+)}{K_a(K_{a,app} + a_H^+)} \quad (17)$$

Let us consider the two most important and illustrative cases including also the the boundary conditions of equation (16) validity. The case (*a*) corresponds to the

* Values d^+ and $d^\pm$ were determined as $d^+ = M^+/V_m^+$ and $d^\pm = M^\pm/V_m^\pm$ where M^+ and $M^\pm$ molecular weight of single molecules of cationic and zwitter-ionic surfactants.

Table 3. Micellar effects of functional detergents in cleavage of 4-nitrophenyl diethyl phosphate **I**, 4-nitrophenyl ethyl ethylphosphonate **II**, and 4-nitrophenyl tosylate **III** in zwitter-ionic micelles of 1-cetyl-3-(2-oximinopropyl)imidazolium **IVa**, 1-cetyl-3-(2-amino-2-oximinoethyl)imidazolium **VIa**, 1-cetyl-3-(2-oxaminoethyl-2-one)imidazolium **VIIIa**, and in combined micelles functional detergent /CTAC

Substrate	ω[a]	α_S[b]	$\alpha_{(R')RIm^+Nu^-}$[c]	Detergent											
				IVa				**VIa**				**aVIII**			
				Δ_1	Δ_2	Δ_3	Δ[d]	Δ_1	Δ_2	Δ_3	Δ[d]	Δ_1	Δ_2	Δ_3	Δ[d]
I	1.0	<<1	?1.0	1.0	560	1.0	560	0.63	560	1.0	350	1.15	560	1.0	620
	1.0	<<1	<0.1	1.0	560	0.12	67	0.63	560	0.13	463	1.15	560	0.30	205
	0.048	<<1	<0.1	0.74	800	5.9	3500	0.48	850	8.0	300	0.73	850	6.8	4800
II	1.0	<<1	?1.0	1.7	520	1.0	880	1.8	580	1.0	1040	1.3	520	1.0	620
	1.0	<<1	<0.1	1.7	520	0.12	110	1.8	580	0.13	0140	1.3	520	0.30	200
	0.091	<<1	<0.1	1.3	710	5.9	5400	–	–	8.0	–	–	–	6.8	–
	1.0	<<1	?1.0	2.0	6600	1.0	13200	0.85	6600	1.0	5600	0.45	6400	1.0	2900
III	1.0	<<1	<0.1	2.0	6600	0.12	1600	0.85	6600	0.13	730	0.45	6400	0.30	860
	0.048	<<1	<0.1	1.53	8250	5.9	75000	1.0	8250	8.0	66000	0.21	8500	6.8	12200

[a] ω is the fraction of functional detergent in combined micelles functional detergent/CTAC.

[b] α_S is the fraction of substrate transferred into the micellar pseudophase.

[c] $\alpha_{(R')RIm^+Nu^-}$ is the fraction of ionized functional detergent or methyl analog.

[d] Calculated by equation (19).

acidity of the medium where the functional detergent and its methyl analog are completely ionized, and at $K_a \gg a_{H^+} \ll K_{a,app}$ equation (17) is transformed into:

$$\Delta = \Delta 1\, \Delta 2 = \frac{k_2^m}{k_2^w} \frac{P_S\ C_4 \omega}{[R'Im^+Nu^-]_0(1 + K_S C)} \qquad (18)$$

The first multiplier in equation (18) $\Delta_1 = k_2^m/k_2^w$ characterizes the effect of medium on the rate of the S_N2-reaction in going from the water to the micellar phase. As seen from the data of Table 3 the Δ_1 values are close to 1 and thus the difference in the free energy of activation for reactions proceeding in the micelles of the functional detergents RIm^+Nu^- and combined micelles RIm^+Nu^-/CTAC ($\Delta G_m^{\neq}$) as compared to those occurring in water ($\Delta G_w^{\neq}$) are negligibly small. The micellear medium does not change the energy barriers of the reaction studied, and $\Delta\Delta G^{\neq} = \Delta G G_m^{\neq} - \Delta G G_w^{\neq} \approx 0$. These results are in agreement with numerous data obtained for a number of functional detergents and system of combined micelles [21, 22, 24]. The second multiplier $\Delta_2 = (P_S C\, \omega)/\{[R'Im^+Nu^-]_0(1 + K_S C)\}$ describes the effect of the substrate concentrating. When the fraction of the bound substrate is small,* and $K_S C << 1$ and $\alpha_S << 1$ the contribution of the concentrating effect to Δ is maximal, and for substrates **I–III** it amounts to $\Delta_2 = P_S$ as is observed at $[R'Im^+Nu^-]_0 \approx C\omega \approx$ CCMF (Table 3).

* Fraction of substrate bound by micelles of surfactant was calculated from expression $\alpha_S = K_S C/(1 + K_S C)$.

With the growing fraction of the bound substrate $0.1 \le \alpha_S \le 0.9$ the contribution of the concentrating effect $\Delta_2 = P_S/(1 + K_S C)$ into Δ value remains the principal, although it decreases with the increase in the concentration of RIm^+Nu^- transferred into micelles. Finally at complete binding of the substrate $K_S C \gg 1$ and $\alpha_S \to 1$ the rate of reaction in water for the methyl analog $R'Im^+Nu^-$ can become equal to the rate of esters **I – III** decompositon in micelles RIm^+Nu^-.

This situation comes true only in case $[R'Im^+Nu^-]_0 = (k_2^m/k_2^w)[RIm^+Nu^-]_m$, i.e. at $\omega = 1$ $[R'Im^+Nu^-]_0 =$ 2–4 mol l^{-1}. It is impossible to make water solution of $R'Im^+Nu^-$ with this concentration, and therefore it is clear that it cannot compete as nucleophiles with the micelles of detergent RIm^+Nu^- in reactions of cleavage of substrates **I–III**.

Case (*b*) corresponds to the acidity of medium where RIm^+NuH and $R'Im^+NuH$ are ionized insignificantly, and at $K_a \ll a_{H^+} \gg K_{a,app}$ equation (17) transforms into (19).

$$\Delta = \Delta 1 \cdot \Delta 2 \cdot \Delta 3 = \frac{k_2^m}{k_2^w} \cdot \frac{P_S C \omega}{[R'Im^+NuH]_0(1 + K_S C)} \frac{K_{a,app}}{K_a} \qquad (19)$$

No matter how the substrate is bound by micelles the contributions Δ_1 and Δ_2 Δ are just the same as in case (*a*), and we should only estimate the dimension of

the contribution from the third multiplier $\Delta_3 = K_{a,app}/K_a$, that results from the change in pK_a at transfer of the functional detergent from water into the micelles of cationic surfactant. The transfer of the reaction into the zwitter-ionic micelles RIm^+Nu^- results in values $\Delta_3 < 1$, and reduction in the cleavage rate of esters **I–III** reaches ~8 times for **IVa**, **VIa**, and ~3 times for **VIIIa**. The transfer of detergents **IV**, **VI**, and **VIII** into the micelles of the cationic surfactant produces the opposite effect, and the favorable change in values $\Delta_3 > 1$ ensures 6–8-fold acceleration of cleavage of these substrates. Actually the transfer of the zwitter-ionic form RIm^+Nu^- from the zwitter-ionic micelles into the micelles of CTAC results in the rate gain of 50 **IVa**, 60 **VIa**, and 20 **VIIIa** times originating from the corresponding increase in the concentration of the reactive form RIm^+Nu^-. In essence, here occurs the "trivial" predominant concentrating of the RIm^+Nu^--forms by cationic micelles of CTAC as compared to the zwitter-ionic micelles of **IVa**, **VIIa**, and **VIIIa**. As follows from equation (20), the maximum possible acceleration of the substrate cleavage in the micelles of surfactant compared to the reaction in water should occur at $K_S C \ll 1$, $[R'Im^+NuH]_0 = \omega C$ and limiting values of $K_{a,app}/K_a = \Delta_3$.

$$\Delta = \frac{k_2^m}{k_2^w} P_S \quad \frac{K_{a,app}}{K_a} \qquad (20)$$

Actually, just under these conditions the transfer of the reaction into the CTAC micelles is accompanied with very large changes in Δ values amounting for ester **III** to 75 000 (**IVa**), 66 000 (**VIa**) and 12 200 (**VIIIa**) times, and for ester **I** to 3500 (**IVa**), 3300 (**VIa**), and 4800 (**VIIIa**) times respectively (Table 3).

The analysis of equation (17) that accounts for the contributions of changes in reactivity, effects of substrate concentrating, and of changes in pK_a permits a conclusion: in the cleavage of esters in micelles RIm^+Nu^- or combined micelles RIm^+Nu^-/CTAC the main factor governing the micellar effects of the functional detergents is the substrate concentrating effect in the phase of individual and combined micelles. This effect is directly affected by the distribution factors: the larger the distribution factor, the greater acceleration. The difference in the distribution factors shows the change in standard free energy of substrates at their transition from water into the micelle medium, for $\Delta G_S^0 = G_{S,m}^0 - G_{S,w}^0 = -RT\ln P_S$. Thus, regardless of the molar composition of the combined micelle RIm^+Nu^-/CTAC occurs decrease in the free energy of esters **I–III**, and the maximum change is found for the most hydrophobic substrate **III** amounting to ΔG_S^0 (**III**) = –5.3 kcal mol^{-1} whereas for the organophosphorus compounds it is smaller: ΔG_S^0 (I) = –3.9 kcal mol^{-1} and ΔG_S^0(**II**) = –3.8 kcal mol^{-1}.*

Inasmuch as esters **I–III** are electroneutral polar compounds, and their solubility changes in the series (**III**) < (**I**) ≈ (**II**) it should be realized that the driving force of the concentrating effect are the hydrophobic interactions ensuring transfer from water into the micelles RIm^+Nu^- and combined micelles RIm^+Nu^-/CTAC both of substrate and nucleophiles, namely, detergent RIm^+Nu^-. Usually the contribution of the reagents concentrating into the observed Δ value reached no less than 95%.

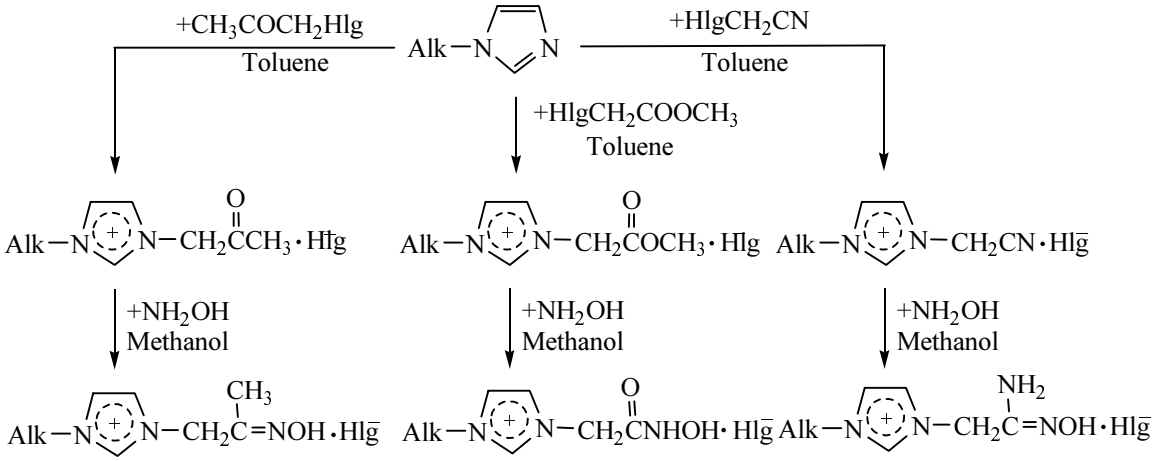
The general character of equation (17) provides a possibility of comparative analysis of the kinetic behavior of functional detergents belonging to different classes, and a necessary and sufficient condition thereof is the knowledge of k_2^m, K_S , and $K_{a,app}$ values for detergents and k_2^w and K_a for their methyl analogs, i.e. compounds incapable of micelles formation. We have formerly demonstrated [15, 16] with the use of an expression like equation (17) that detergent **IVa** containing covalently bonded oximate group is a more powerful nucleophile than 1-dodecyl-3-oximinomethylpyridinium iodide **X** which is considered to be among the most efficient functional detergents for the cleavage of organophosphorus compounds [25]. We were unable to carry out a comparative analysis in the framework of equation (17) of micellar effects of detergents **IVa**, **VIa**, and **VIIIa** with those of zwitter-ionic forms of 1-dodecyl-3-oximinomethylpyridinium halides **Xa** [25], 1-cetyl-3-oximino-methylpyridinium bromide **XIa** [or 1-cetyl-(2 or 4)-oximinomethylpyridinium halides] [26], and 5-[*N*-cetyl-*N,N*-dimethyl-*N*-(β-ethoxy)]ammonium-2-iodosobenzoate **xIIa** [27, 28] for the effect of the micellar phase on the acid-base properties of compounds **Xa-XIIa** is not quite clear. Therefore the estimation of the micellar system efficiency in the ester **I** cleavage was done by comparison of k_{app}, s^{-1}, values measured under identical conditions. Among the three isomeric detergent on the pyridinium basis the most active proved to be 1-cetyl-3-oximinomethylpyridinium bromide **XIa**, and zwitter-ionic micelles of **XIa** at $C = 1.5 \times 10^{-4}$ mol l^{-1} and pH = 10 bound the organophosphorus substrate virtually completely. This corresponds to and

* ΔG_S^0 values for ester **I–III** are mean values with errors not exceeding 10% calculated using distribution factors P_S, listed in Table 1.

$K_S > 10^5$ l mol^{-1}, then the driving force of substrate **I** transfer from water into the micellar phase remains unclear. Ester **I** is hardly a very hydrophobic substrate, it is rather the opposite, for it is characterized by values $K_S \approx 100–300$ lmol^{-1} [14, 16, 25], whereas for 4-nitrophenyl diphenyl phosphate which is a truly hydrophobic organophosphorus compound $K_S \geq 10^4$ l mol^{-1} [22]. On the other hand, the pH-profile of the reaction demonstrates the following: in the range of pH = 8.5–10.0 the cleavage rate increases 1.5-fold, then occurs pH-independent phosphorylation of zwitter-ionic detergent **XIa**. This pH-profile corresponds to the acid ionization constant for **XI** $pK_{a,app} \leq 8.5$ whereas its methyl analog has $pK_a \approx 9.5$ [6]; it means that in the micellar phase $pK_{a,app}$ for detergent **XIa** is smaller than this value in water, although for the detergent of a like structure **X** $pK_a \approx pK_{a,app}$ [25], and for detergentов **IVa**, **VIa**, and **VIIIa** the observed pattern is opposite, and $pK_a < pK_{a,app}$ (Table 3). And finally, the nucleophilicity of the oximate moiety of **xIa** in its micelles $k_2^m = k_{app,max}V_m = 5.32 \times 10^{-6} \times 0.5 = 2.66 \times 10^{-6}$ l mol^{-1} s^{-1} is less than in water [6] nearly 1000 times. No such decrease in the nucleophilicity of zwitter-ionic surfactant forms with respect to electroneutral moderately hydrophobic substrates was not observed. Detergent **XIa** does not at all accelerate the cleavage of ester **I** for its methyl analog reacts at the rate $k_{app} \geq 10^{-6}$ s^{-1} [6]. These kinetic and thermodynamic parameters of the reaction between detergent **XIa** and ester **I** are difficult to interpret within the framework of the simple pseudophase distribution model, and thus to apply them to calculation of Δ values and to comparison of micellar effects of **IVa**, **VIa**, and **VIIIa** with those of **XIa** is hardly useful. Nonetheless, we will do it with a certain caution. For instance, at $\alpha_S \approx 1.0$ the cleavage rate of ester **I** in micelle **IVa** $k_{app} = 1.6 \times 10^{-3}$ s^{-1}, and for micelle **XIa** $k_{app,max} = 5.32 \times 10^{-6}$ s^{-1}, and thus detergent **IVa** ~ 3000 times faster reacts with organophosphorus compound than the zwitter-ionic micelles **XIa**. A similar acceleration of reaction, ~ 4100 times, is observed for **VIa**, and for micelles of the least basic detergent **VIIIa** the acceleration is ~ 700 times. Hence the advantage of detergents **IVa**, **VIa**, and **VIIIa** before **XIa** for the cleavage of organophosphorus compounds is obvious.

Zwitter-ion detergent **xIIa** as a true nucleophilic catalyst cleaves ester **I** at a rate $k_{app} = 3.4 \times 10^{-3}$ s^{-1} [27, 28], whereas detergents **IVa** and **VIa** react with the same substrate at a rate $k_{app} = 1.6 \times 10^{-2}$ and 2.2×10^{-2} s^{-1} respectively, and in the case of detergent **VIIIa** reaction occurs with a comparable rate. It should be noted however that detergent **XIIa** reacts with ester **I** in a combined micellar system with CTAC, and the function of substrate binding is performed by micelles of cationic CTAC. Detergent **xIIa** proper is insoluble in water, and therefore it can hardly be regarded as efficient nucleophilic detergent.

Hence the new functional detergents **IVa, VIa**, and **VIIIa** containing in the head part an imidazolium ring and covalently linked thereto fragments of typical α-nucleophiles (oximate, amidoximate, and hydroxamate moieties) serve as a basis of unique supernucleophilic micellar systems ensuring exclusively high rates for cleavage of organophosphorus compounds caused by "trivial" effect of reagents concentrating.



EXPERIMENTAL

4-Nitrophenyl diethyl phosphate (**I**), 4-nitrophenyl ethyl ethylphosphonate (**II**), 4-nitrophenyl -tosylate (**III**) were prepared by 4-nitrophenol acylation by procedure described in [29]. Methyl iodide, cetyl bromide, chloroacetone, chloroacetonitrile methyl chloroacetate, and imidazole were commercial products subjected to purification by standard methods. Bromoacetone was prepared and purified as in [30]. Cetyltrimethylammonium chloride was synthesized and purified according to [31].

Halides of 1-methyl-3-(2-oximinopropyl)imidasolium, 1-methyl-3-(2-amino-2-oximino-ethyl)imidazolium, 1-methyl-3-(2-oxaminoethyl-2-one)imidazolium, 1-cetyl-3-(2-oximinopropyl)-imidazolium, 1-cetyl-3-(2-amino-2-oximinoethyl)imidazolium, and 1-cetyl-3-(2-oxaminoethyl-2-one)imidazolium were prepared according to a general method we developed as shown on the scheme.

First the imidazole was alkylated with methyl iodide or cetyl bromide, then into the 1-alkylimidazole was introduced a carbonyl, cyano, or ester group. The corresponding oximes, amidoximes, or hydroxamic acids were obtained at treating the ketones, nitriles, and esters with free hydroxylamine in methanol [32–34]. On removing the solvents oximes **V**, amidoximes **VII**, and hydroxamic acids **IX** were 2-3 times recrystallized from 2-propanol, and detergents **IV, VI, VIII** from ethanol– ethyl ether mixture.*

Inorganic reagents of "specially pure" or "chemically pure" grade were used without additional purification.

All solvents were prepared with double distilled water before every series of kinetic measurements. The analytical concentrations of oxime **V**, amidoxime **VII**, and hydroxamic acid **IX** were so that the reagents solutions were simultaneously buffers. The ionic strength was supported by adding 1 mol l^{-1} of KCl. In the presence of detergents **IV, VI**, and **VIII** the ionic strangth of solutions was not fixed. In all experiments the required pH value was adjusted with the use of concentrated solutions of potassium hydroxide or hydrochloric acid. The acidity of the reaction medium was determined before and after each kinetic run on pH-meters OP-205 и OP-213 (Radelkis, Hungary). When the pH during the experiment changed by more than 0.05 pH units, the result of the run was rejected

The cleavage of substrates **I–III** with nucleophilic reagents **IVa–IXa** in water at various pH values occurs with formation of 4-nitrophenolate ion as one of the reaction products. Therefore the reaction progress was monitored by accumulation of 4-nitrophenolate ion (l = 400–430 nm) measured on spectrophotometer Specord UV VIS at 25±0.5°C. The rate constants of pseudofirst order (k_{app}, s^{-1}) were determined from the change in absorption with time (equation 21):

$$\ln(D_\infty - D_t) = \ln(D_\infty - D_0) - k_{app}t \qquad (21)$$

where D_0, D_t, and D_∞ is absorption in time $t = 0$, $t = t_i$, and at completion of the reaction. In all cinetic measurements the initial concentration of substrates **I–III** was considerably smaller than the initial concentration of nucleophile.

The CCMF values were determined by the method of difference UV spectroscopy with the use of fluorescein (λ = 507 nm) [35] and from kinetic data. In the case of ester **III** cleavage by functional micelles RIm^+Nu^- the CCMF values were estimated from kinetic data [4] with the use of procedures of mathematical statistics [36].

*^{1}H NMR data and melting points can be obtained from the authors.

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