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Micelle Effects of Functionalized Surfactants, 1-Cetyl-3-(2-hydroxyiminopropyl)imidazolium Halides, in Reactions with *p*-Nitrophenyl *p*-Toluenesulfonate, Diethyl *p*-Nitrophenyl Phosphate, and Ethyl *p*-Nitrophenyl Ethylphosphonate

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Abstract—1-Cetyl-3-(2-hydroxyiminopropyl)imidazolium chloride and bromide were synthesized for the first time. These compounds are functionalized zwitterionic surfactants which give rise to micelle formation in aqueous solution. Kinetic and thermodynamic analysis of nucleophilic cleavage of *p*-nitrophenyl *p*-toluenesulfonate, diethyl *p*-nitrophenyl phosphate, and ethyl *p*-nitrophenyl ethylphosphonate in the presence of 1-cetyl-3-(2-hydroxyiminopropyl)imidazolium halide micelles showed that the latter are powerful nucleophilic reagents whose kinetic behavior can be described in terms of a simple pseudophase distribution model. The efficiency of substrate solubilization with zwitterionic surfactant micelles and the reactivity of the oxime fragment in the micelle phase were estimated on a quantitative level. The observed acceleration of S_N2 reactions with the examined *p*-nitrophenyl esters relative to analogous reactions of zwitterionic 1-methyl-3-(2-hydroxyiminopropyl)imidazolium halides is, respectively, 12800, 550, and 900 times; it is explained mainly by increased concentration of the reactants in micelles.

Micelle effects represent the most prominent and extensively studied example of surfactant influence on the kinetics of organic reactions in water and aqueous–organic mixtures. These systems open wide prospects for controlling the rate of chemical transformations and the state of equilibria therein [1–3]. Acceleration of organic reactions in micelle solution is determined mainly by two factors: (1) concentration of the reactants in the micelle pseudophase and (2) possible considerable increase in the reaction rate in going from aqueous solution to surfactant micelles [4]. Cationic micelles accelerate reactions of anionic nucleophiles with neutral substrates (including those classed with ecotoxicants) [5–7]. One of the most promising ways of modification of cationic surfactant molecules includes introduction into the head part of functional groups capable of forming highly reactive anionic species, e.g., fragments of α-nucleophiles, such as oximate [8–13], hydroxamate [13–17], hydroperoxide [18], etc. [19, 20]. An obvious advantage of such surfactants is that the role of nucleophilic reagent is played just by the functionalized zwitterionic surfactant which gives rise to micelle formation. Here, the problem of binding of anionic nucleophile with micelles is eliminated: regardless of the nature of specific group, even at the lowest possible micelle concentration, the "local" concentration of anionic nucleophilic species in the micelle phase is as high as possible for a given system [12].

In the present work we performed a detailed kinetic analysis of nucleophilic cleavage of ecotoxic *p*-nitrophenyl *p*-toluenesulfonate (**I**), diethyl *p*-nitrophenyl phosphate (**II**), and ethyl *p*-nitrophenyl ethylphosphonate (**III**) in the presence of 1-cetyl-3-(2-hydroxyiminopropyl)imidazolium halides (**IV**) which are new functionalized surfactants whose head part includes

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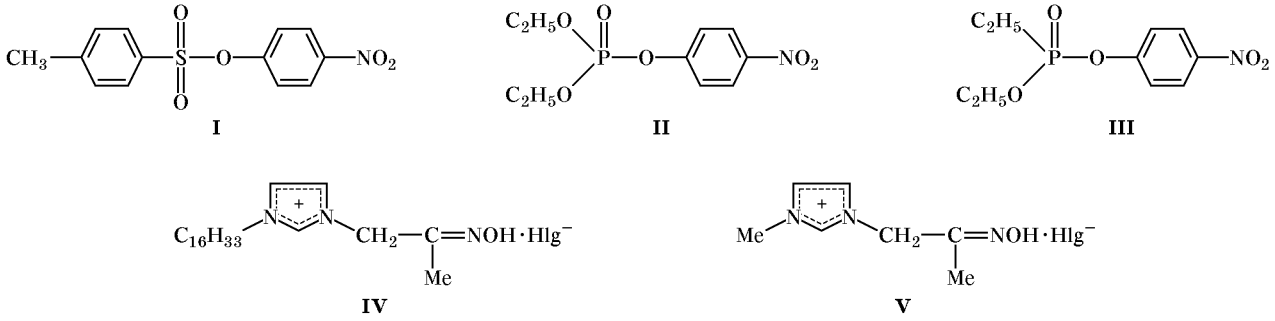


I **II** **III**

IV **V**

Hlg = Cl, Br.

an imidazolium ring and hydroxyimino group, as well as in the presence of 1-methyl analogs **V**, in water at 25°C. Our study was aimed at establishing the nature of factors responsible for the high rates of these processes, namely (1) change of the reactivity in going from aqueous to micelle phase and/or (2) effect of reactant concentration in the micelle phase.

Oximate ions (Ox^-) are typical α-nucleophiles which rapidly react with various substrates, such as carboxylic, phosphoric, phosphonic, and sulfonic acid esters [21–26]. The kinetic behavior of zwitterionic species **Va**, generated from 1-methyl-3-(2-hydroxyiminopropyl)imidazolium chloride or bromide according to Scheme 1, in reactions with substrates **I**–**III** follows analogous general relations. The reaction of oximate ion **Va** with esters **I**–**III** in water (Scheme 2) includes nucleophilic attack on the electron-deficient center in the substrate by anionic oxime species to give the corresponding *O*-acyl derivatives [25].

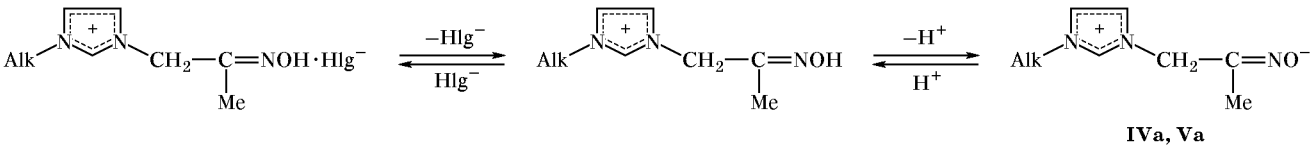
The dependence of the apparent pseudofirst-order rate constant k_{ap} (s^{-1}) on the overall oxime concentration $[HOx]_0$ (M) is typical of processes in which the reactive species is the major buffer component (Ox^-). The reaction rate increases with rise in both nucleophile concentration (Fig. 1a) and pH (pH profile, Fig. 1b). The rate constant is described by Eq. (1):

$$k_{ap} = k_2 \alpha_{OX^-} [HOx]_0 = k_2 [Ox^-], \quad (1)$$

where $\alpha_{OX^-} = K_a/(K_a + a_{H^+})$ is the fraction of oximate ion, and K_a is the acid ionization constant of the oxime. The values of k_{ap} were corrected for the contribution of alkaline hydrolysis, $k_{OH^-} a_{OH^-}$, if it exceeded 5%. The second-order rate constant k_2, $l\ mol^{-1}\ s^{-1}$, which characterizes the nucleophilic reactivity of zwitterion **Va**, was determined from the linear dependence of k_{ap} versus $[Ox^-]$. Zwitterionic species **Va** derived from 1-methyl-3-(2-hydroxyiminopropyl)imidazolium chloride or bromide shows no anomalies in the kinetic behavior, and its reactivity conforms to the Brønsted equation for the reaction of oximate ions with esters **I**–**III** [23].

1-Cetyl-3-(2-hydroxyiminopropyl)imidazolium chloride and bromide in aqueous solution give rise to two kinds of reactive micelles: mixed micelles formed by molecules **IV** and **IVa** and those consisting of only zwitterionic species **IVa**. The nucleophilic center in the latter is located in the oximate moiety. This

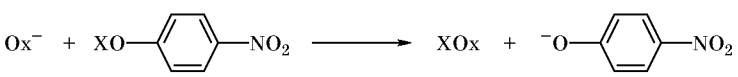
Scheme 1.



IVa, Va

IV, Alk = $C_{16}H_{33}$; **V**, Alk = Me.

Scheme 2.



X = Ts, $(EtO)_2P(O)$, $Et(EtO)P(O)$.

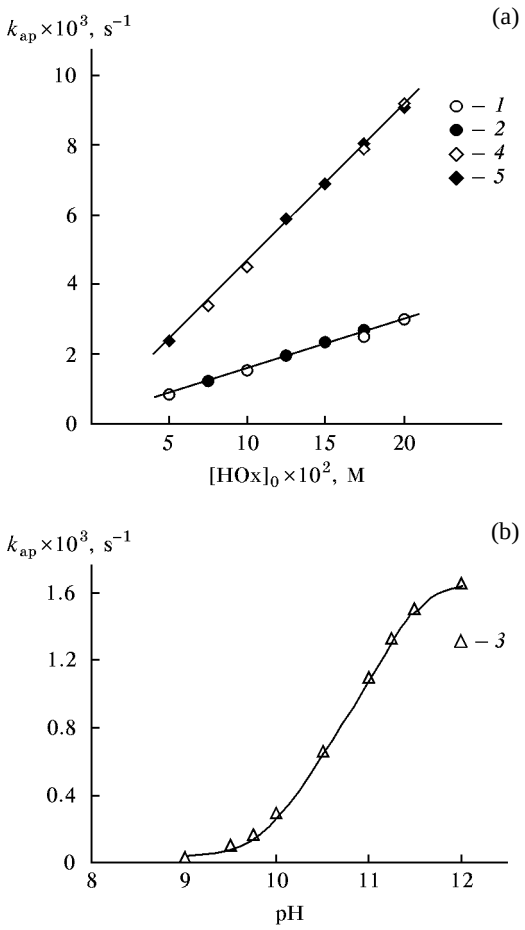


Fig. 1. Nucleophilic cleavage of (*1*, *2*) *p*-nitrophenyl *p*-toluenesulfonate (**I**), (*3*) diethyl *p*-nitrophenyl phosphate (**II**), and (*4*, *5*) ethyl *p*-nitrophenyl ethylphosphonate (**III**) with zwitterionic form **Va** of 1-methyl-3-(2-hydroxyiminopropyl)imidazolium halides; water, 25°C, μ = 1.0 (KCl). (a) Concentration dependences for the reactions of *p*-nitrophenyl *p*-toluenesulfonate (**I**), pH 12.0, and ethyl *p*-nitrophenyl ethylphosphonate (**III**), pH 10.7, with 1-methyl-3-(2-hydroxyiminopropyl)imidazolium halides (**Va**); (b) pH dependence for the reaction of diethyl *p*-nitrophenyl phosphate (**II**) with 1-methyl-3-(2-hydroxyiminopropyl)-imidazolium halides (**Va**); $[HOx]_0$ = 0.2 M. Point numbers *1*, *3*, and *4* correspond to the reactions with 1-methyl-3-(2-hydroxyiminopropyl)imidazolium chloride, and *2* and *5*, with bromide.

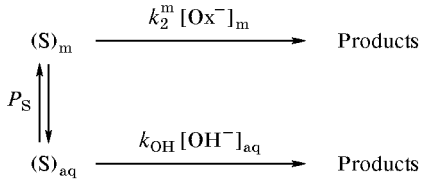
follows from the pH profiles for reactions with substrates **I** and **II**, shown in Fig. 2. Up to pH ≈ 12.5, the rate of transfer of *p*-tolylsulfonyl and diethoxyphosphinoyl groups to the oximate fragment increases with rise in pH. This pattern indicates that nucleophilic cleavage of the substrates occurs in mixed micelles **IV**/**IVa**. The dependence then comes to a plateau, and at pH > 12.5 the apparent rate constant corresponds to the reaction occurring in zwitterionic micelles formed by **IVa**. Therefore, the kinetics of these processes were studied at pH 12.9 (at pH 12.6 for ester **III**), i.e., when substrates **I**–**III** undergo nucleophilic cleavage only in zwitterionic micelles.

The concentration profiles of these reactions are more complex (Fig. 3). In the case of esters **II** and **III**, only alkaline hydrolysis* was observed up to critical micelle concentration; as the micelle concentration rose, the reaction rate considerably increased. When the substrate is completely bound with micelles of **IVa**, the reaction rate no longer depends on the surfactant concentration, and k_{ap} tends to k_{max} (plateau in Fig. 3a). It should be noted that at pH 12.9 the concentration dependence (as well as the pH dependence) includes points for 1-cetyl-3-(2-hydroxyiminopropyl)-imidazolium chloride and bromide. This means that a common concentration dependence exists, indicating the absence of inhibitory effect of halide ions on the reaction under study (cf. [9]). An analogous concentration profile is observed for substrate **I** (Fig. 3a, 3b). However, the rate of cleavage of ester **I** strongly increases before reaching the critical micelle concentration (2.4×10^{-4} M, Fig. 3b), which was determined by independent experiments using difference UV spectroscopy. An analogous CMC value was obtained by treatment of the kinetic data for reactions of esters **II** and **III** with micelles **IVa** (Fig. 3b, Table 1). For example, at a surfactant concentration c_0 of 8.06×10^{-5} M, the contribution of alkaline hydrolysis being less than 10%, the reaction rate in water is higher by a factor of ~4000 [k_{ap}(**IVa**)/k_{ap}(**Va**)] than the rate of the reaction with 1-methyl analog. Such increase in the reaction rate is likely to result either from formation of highly reactive premicelles or from decrease in CMC induced by ester **I** which is more hydrophobic than **II** and **III** [27]. Presumably, the latter factor should be preferred, for (1) it remains unclear why premiceles (if they are formed) rapidly react with ester **I** but slowly with **II** and **III** and (2) the formation of premicelles should give a distinct maximum on the concentration profile at c_0 < CMC [27], which is not observed (Fig. 3b). Using the mathematical statistics methods [28] (see Experimental), the critical micelle concentration for the reaction of **I** with **IVa** was estimated at 5.40×10^{-5} M. This value provides a good agreement between the calculated dependence of k_{ap} on c_0 and experimental concentration profile for the reaction of ester **I** with micelles **IVa**. We can conclude that 1-cetyl-3-(2-hydroxyiminopropyl)imidazo-

* Undoubtedly, monomeric **IVa** species also react with esters **I**–**III** in water, but the contribution of this pathway is negligible as compared to alkaline hydrolysis.

lium halides **IV** in aqueous solution give rise to only one kind of reactive species, namely micelles formed by zwitterions **IVa**. The observed considerable qualitative and quantitative differences in the kinetic behavior of micelles formed by zwitterionic species **IVa** and **Va** (cf. Fig. 1 and Figs. 2, 3) may be interpreted in terms of the simple pseudophase model of micelle formation [4], according to which substrate S is rapidly distributed between two phases: micelle pseudophase (m) and aqueous phase (aq) (Scheme 3).

Scheme 3.



The equilibrium is controlled by the distribution coefficient P_S [Eq. (2)], and the chemical reaction *per se* does not affect the thermodynamics of substrate distribution.

$$P_S = [S]_m/[S]_{aq}. \quad (2)$$

Taking into account the above stated, the current substrate concentration [S], M, is the sum of substrate concentrations in the micelle and aqueous phases, averaged by the overall volume of the reaction system:

$$[S] = [S]_m\, c\, V + [S]_{aq}\, (1 - c\, V), \quad (3)$$

where V, l/mol, is the partial molar volume of micelles formed by zwitterionic surfactant, $c = c_0 -$ CMC, M, is the micelle concentration, and $c\,V$ and $(1 - c\,V)$ are the volume fractions of the micelle pseudophase and aqueous phase, respectively. Joint solution of Eqs. (2) and (3) gives

$$[S]_m = \frac{P_S[S]}{1 + (P_S - 1)c\,V}, \quad (4)$$

$$[S]_{aq} = \frac{[S]}{1 + (P_S - 1)c\,V}. \quad (5)$$

Nucleophilic cleavage of a substrate in aqueous solutions of 1-cetyl-3-(2-hydroxyiminopropyl)imidazolium halides follows two concurrent pathways shown in Scheme 3: in the micelle pseudophase, S_N2 reaction with the oximate fragment of **IVa** occurs, while in the aqueous phase the substrate undergoes

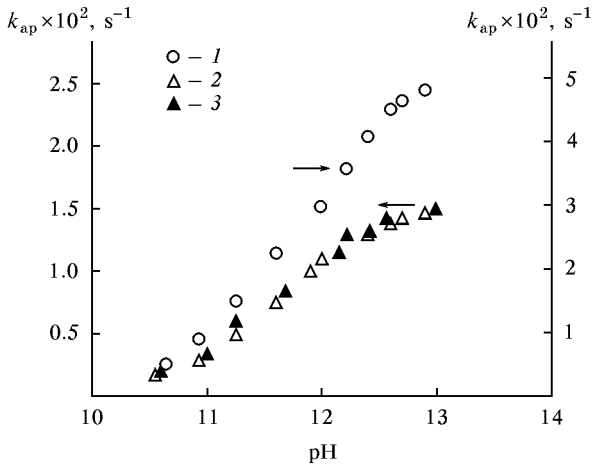


Fig. 2. pH profiles for the reactions of (*1*) *p*-nitrophenyl *p*-toluenesulfonate (**I**), c_0 = 0.001 M, and (*2*, *3*) diethyl *p*-nitrophenyl phosphate (**II**), c_0 = 0.02 M with 1-cetyl-3-(2-hydroxyiminopropyl)imidazolium (*1*, *2*) chloride and (*3*) bromide **IVa**; water, 25°C.

alkaline hydrolysis. The rates of these processes are described by Eqs. (6) and (7), respectively.

$$\nu_m = k_2^m[Ox^-]_m[S]_m = k_2^m(1/V)[S]_m = k_m[S]_m; \quad (6)$$

$$\nu_{aq} = k_{OH}[OH^-]_{aq}[S]_{aq} = k_{OH}^{aq}[S]_{aq}. \quad (7)$$

The overall rate of the process is described by the following equation:

$$\nu = \nu_m\, c\, V + \nu_{aq}(1 - c\, V). \quad (8)$$

By substituting Eqs. (4)–(7) into (8), we obtain formula (9) for the apparent pseudofirst-order rate constant:

$$k_{ap} = \frac{\nu}{[S]} = \frac{k_m P_S\, c\, V + k_{OH}^{aq}(1 - c\, V)}{1 + K_S\, c}, \quad (9)$$

where $K_S = (P_S - 1)V \approx P_S\, V$, mol/l. The quantity K_S has a dimensionality of the equilibrium constant for binding of substrate with zwitterionic surfactant **IVa** micelles. Insofar as Eq. (9) was derived without any simplifying assumptions, it provides the possibility for analyzing the character of micelle effects with regard to the reaction conditions, efficiency of binding of substrates **I**–**III**, and ratio of the second-order rate constants in the micelle and aqueous phases.

The situation when a substrate is either weakly bound or is not bound at all by functionalized surfactant micelles, i.e., when $P_S \le 1$, is unusual. On the other hand, it demonstrates the significance of the

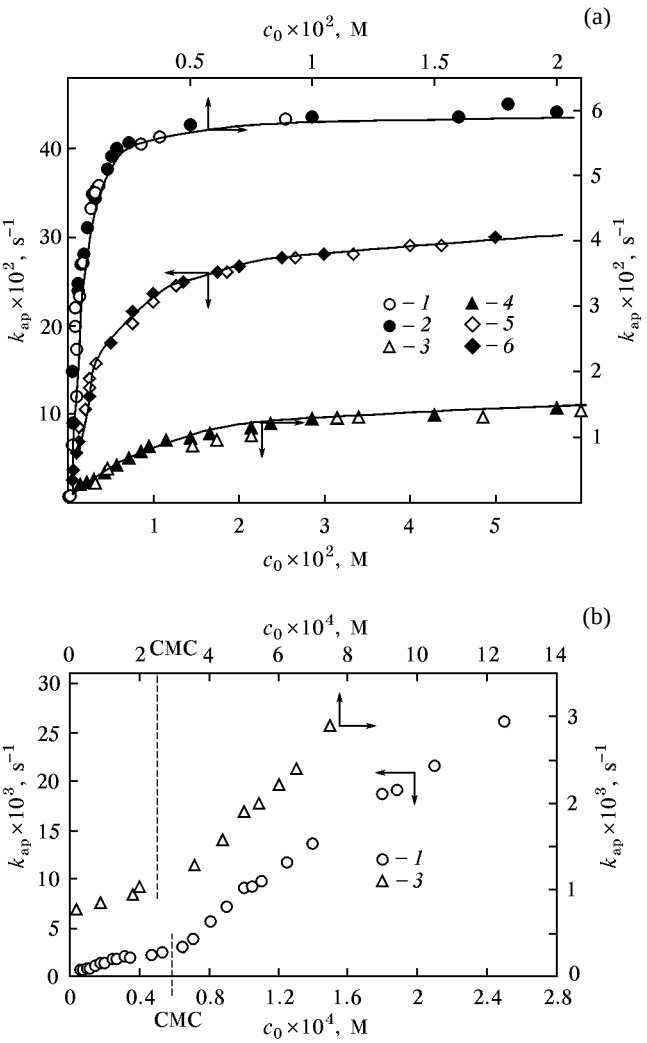


Fig. 3. Concentration dependences of the apparent pseudo-first-order rate constants for the reactions of (*1*, *2*) *p*-nitrophenyl *p*-toluenesulfonate (**I**), (*3*, *4*) diethyl *p*-nitrophenyl phosphate (**II**), and (*5*, *6*) ethyl *p*-nitrophenyl ethylphosphonate (**III**) with 1-cetyl-3-(2-hydroxyiminopropyl)imidazolium (*1*, *3*, *5*) chloride and (*2*, *4*, *6*) bromide (**IVa**); water, 25°C. (a) *p*-Nitrophenyl *p*-toluenesulfonate (**I**), pH 12.9; diethyl *p*-nitrophenyl phosphate (**II**), pH 12.9; ethyl *p*-nitrophenyl ethylphosphonate (**III**), pH 12.6. (b) Initial parts of the k_{ap}—c_0 plots for the reactions of *p*-nitrophenyl *p*-toluenesulfonate (**I**) and diethyl *p*-nitrophenyl phosphate (**II**) with **IVa** micelles; pH 12.9.

effect of reactant concentration as a factor controlling the rate of micelle reactions. In this case, K_S varies from 0 to $-V$, and Eq. (9) is transformed into (10):

$$k_{ap} = k_m P_S c V + k_{OH}^{aq}. \quad (10)$$

Insofar as $P_S \le 1$ and $c V \ll 1$, the first term in Eq. (10) is negligible. The reaction rate at any concentration c cannot differ from the rate of alkaline hydrolysis of the substrate, i.e., no acceleration should be observed. The reason is that the reactants appear in different phases: the substrate is in the aqueous phase, and the reagent (oximate ion), in the micelle phase. Therefore, only hydrolysis of the substrate occurs.

Quite different kinetic relations are observed when the substrate is well bound by functionalized surfactant micelles. The high efficiency of solubilization of esters **I**–**III** with **IVa** micelles, which follows from relatively low concentration c corresponding to k_{max} (Fig. 3), indicates that $P_S \gg 1$ (Table 1) and $c V \ll 1$. In this case, Eq. (9) may be represented as

$$k_{ap} = \frac{k_m K_S c + k_{OH}^{aq}}{1 + K_S c} = \frac{k_m K_S c}{1 + K_S c} + \frac{k_{OH}^{aq}}{1 + K_S c}. \quad (11)$$

As follows from Eq. (11), micelles of **IVa** exert a dual effect on the apparent reaction rate. On the one hand, they inhibit alkaline hydrolysis so that its rate [the second term in Eq. (11)] decreases as c rises. On the other hand, the rate of substrate cleavage in micelles of **IVa** [the first term in Eq. (11)] sharply increases, which overcompensates the reduced contribution of alkaline hydrolysis. Finally, at $K_S c \gg 1$, almost no alkaline hydrolysis occurs, and the reaction rate [Eq. (12)] reaches its maximal value (plateau on the concentration dependence shown in Fig. 3a).

$$k_{ap} = k_{max} = k_m = k_2^m V^{-1}. \quad (12)$$

Therefore, when the substrate is transferred completely to the micelle pseudophase, the corresponding value of k_m, s^{-1}, which characterizes the reactivity of the oximate fragment in **IVa** at $[Ox^-]_m = 1/V$, may be determined from any point on the plateau in the concentration dependence for esters **I**–**III** (Fig. 3a).

The binding constants K_S for esters **I**–**III** characterize the thermodynamics of equilibrium substrate distribution between the aqueous phase and **IVa** micelles, so that they are necessary for kinetic and thermodynamic description of the reactions under study. The kinetic method provides a simple, convenient, and fairly reliable procedure for quantitative estimation of K_S values. The kinetic data obtained under the conditions when the fraction of the bound substrate α_S was within the range $0.1 < \alpha_S < 0.9$ were treated in two ways. According to the first of these, K_S values for esters **I**–**III** were determined from Eq. 13; simultaneously, k_m values were also determined (Fig. 4a, 4b).

$$k_{ap} = k_m - \frac{k_{ap} - k_{OH}^{aq}}{K_S c}. \quad (13)$$

In terms of the second approach, the binding constants K_S were estimated using k_m values calculated by Eq. (12). For this purpose, Eq. (11) was transformed into (14):

$$\frac{k_{ap} - k_{OH}^{aq}}{k_m - k_{ap}} = K_S c, \quad (14)$$

and the constants K_S were determined from linear dependences (14) plotted in Fig. 5. The values of K_S (Table 1), determined for different reaction conditions, coincided. This indicates the validity of using the kinetic method for determination of binding constants.

Table 1 summarizes the calculated values of k_m and K_S for esters **I**–**III** and the corresponding critical micelle concentrations (CMC). A good agreement between the k_m values calculated from k_{max} and those found using Eq. (13) (Fig. 4) provides a support to the proposed mechanism of nucleophilic cleavage of substrates **I**–**III** (Scheme 3) in zwitterionic micelles **IVa**. The values of k_m and K_S given in Table 1 are apparent quantities. In order to determine the proper nucleophilicity of the oximate fragment in zwitterionic surfactant **IVa** (k_2^m, l mol^{-1} s^{-1}), as well as the distribution coefficients P_S, it is necessary to know the partial molar volume or (more precisely) the volume of that micelle region in which the substrate is localized and where the S_N2 reaction occurs [V_m; Eqs. (15), (16)]:

$$k_2^m = k_m V_m; \quad (15)$$

$$P_S = 1 + K_S/V_m \approx K_S/V_m. \quad (16)$$

In a number of processes involving anionic nucleophiles and neutral substrates in cationic surfactant micelles and co-micelles, the values of k_2^m are comparable to or slightly lower than the second-order rate constants for the same anionic nucleophiles in water [2, 3]. The differences often arise from the choice of V_m. The V_m values for trimethylammonium micelles are usually assumed to range from 0.14 to 0.37 l/mol [13]. Taking into account that zwitterionic surfactant **IVa** has a bulky head moiety and that one of the factors determining V_m is just the volume of the head fragment, the region of **IVa** micelles where esters **I**–**III** are cleaved should be larger than the corresponding region in trimethylammonium micelles. We selected a V_m value of 0.5 l/mol, for just that value

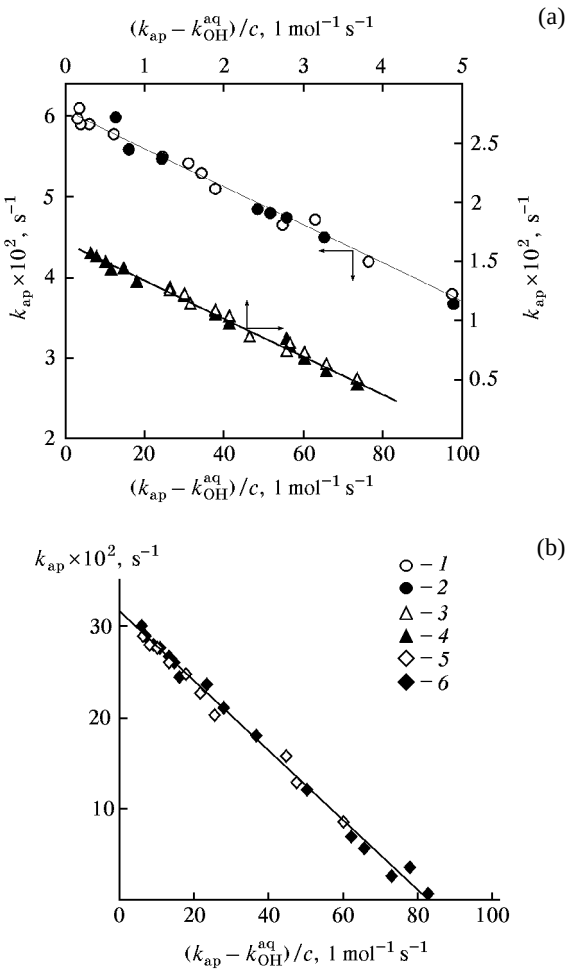


Fig. 4. Plots of the apparent pseudofirst-order rate constants k_{ap}, s^{-1}, versus $(k_{ap} - k_{OH}^{aq})/c$, l mol^{-1} s^{-1}, for the reactions of (*1*, *2*) *p*-nitrophenyl *p*-toluenesulfonate (**I**), (*3*, *4*) diethyl *p*-nitrophenyl phosphate (**II**), and (*5*, *6*) ethyl *p*-nitrophenyl ethylphosphonate (**III**) with micelles formed by (*1*, *3*, *5*) 1-cetyl-3-(2-hydroxyiminopropyl)imidazolium chloride and (*2*, *4*, *6*) bromide; water, 25°C. (a) *p*-Nitrophenyl *p*-toluenesulfonate (**I**), pH 12.9, and diethyl *p*-nitrophenyl phosphate (**II**), pH 12.9. (b) Ethyl *p*-nitrophenyl ethylphosphonate (**III**), pH 12.6.

was used to describe reactions in metal micelles characterized by a considerable size of their head fragments [20]. Using V_m = 0.5 l/mol, we calculated the rate constants k_2^m and distribution coefficients P_S (Table 1) by Eqs. (15) and (16).

Quantitative estimation of micelle effects produced by zwitterionic surfactant **IVa** [Δ in Eq. (17)] implies that factors governing the rate of nucleophilic cleavage of esters **I**–**III** in the micelle phase (i.e., the driving force of the reaction) be known. For this purpose, let us make use of Eq. (17) which sets Δ as the ratio of rate constants for the reactions of **IVa** in

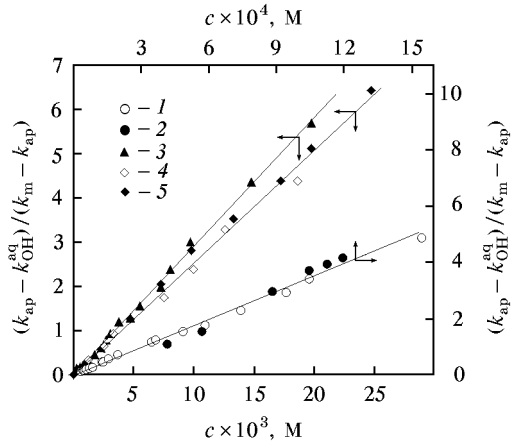


Fig. 5. Plots of $(k_{ap} - k_{OH}^{aq})/(k_m - k_{aq})$ versus c, M, for the reactions of (*1*, *2*) *p*-nitrophenyl *p*-toluenesulfonate (**I**), (*3*) diethyl *p*-nitrophenyl phosphate (**II**), and (*4*, *5*) ethyl *p*-nitrophenyl ethylphosphonate (**III**) with micelles formed by (*1*, *4*) 1-cetyl-3-(2-hydroxyiminopropyl)imidazolium chloride and (*2*, *3*, *5*) bromide; water, 25°C.

the micelle phase [k_{ap}(**IVa**)] and of its methyl analog **Va** [k_{ap}(**Va**)] in water at $[\mathbf{Va}]_0 = c$. We assume that the second-order rate constants for compounds **IVa** and **Va** in water are similar or comparable. This assumption seems to be justified since the inductive effects of the cetyl and methyl groups on the basicity of **IVa** and **Va** are comparable and the slopes of the Brønsted relations for the reactions of oximate ions with esters **I**–**III** and other substrates fall into the β_N range from 0 to 0.2 [23, 26]. The first multiplier in Eq. (17) shows how does the reaction rate change in going to the micelle phase. Insofar as k_2^m/k_2 are equal to 2, 1, and 1.8 for substrates **I**–**III**, respectively (Table 1), the difference in the Gibbs energies of activation for the reactions in the micelle phase ($\Delta G_m^{\neq}$) and in water ($\Delta G_{aq}^{\neq}$) is negligible. Therefore, the micelle phase has no specific stabilizing effect on the transition state. This conclusion is consistent with numerous data obtained for functionalized surfactants and mixed micelle systems [2, 3, 29].

$$\Delta = \frac{k_{ap}(\mathbf{IVa})}{k_{ap}(\mathbf{Va})} = \frac{k_2^m [Ox^-]_m K_S c}{k_2 [\mathbf{Va}]_0 (1 + K_S c)}$$
$$= \frac{k_2^m}{k_2} - \frac{K_S c}{V_m [\mathbf{Va}]_0 (1 + K_S c)}. \quad (17)$$

The second multiplier in Eq. (17) reflects the contribution to Δ of the effect of reactant concentration. When the fraction of the bound substrate $\alpha_S \ll 1$ and $K_S c \ll 1$, this contribution attains its maximal value and is $K_S/V_m = P_S$ for substrates **I**–**III**. Such situation is observed at surfactant concentrations approaching CMC. As the fraction of the bound substrate rises, $0.1 \le \alpha_S \le 0.9$, the contribution of the reactant concentration effect $P_S/(1 + K_S c)$ to Δ remains determining, though it decreases as the concentration of **VIa** micelles increases (Table 2). Finally, at $\alpha_S \to 1$ and $K_S c \gg 1$ the rate of the reaction with methyl analog **Va** is as follows: $k_{ap}(\mathbf{Va}) = (k_2/k_2^m) k_{ap}(\mathbf{IVa})$ for esters **I** and **III** and $k_{ap}(\mathbf{Va}) = k_{ap}(\mathbf{IVa})$ for ester **II**, and the concentration of **Va** becomes equal to the "local" concentration of the oximate fragment in zwitterionic micelles **IVa**: $[\mathbf{Va}]_0 = [Ox^-]_m = 1/V_m = 2$ M. Taking into account the change in the reactivity, the reaction rate in water should be equal to that in the micelle phase at $k_2^m/k_2[Ox^-] = 4$, 2, and 3.6 M for substrates **I**–**III**, respectively. It is impossible to attain such a concentration of the methyl analog, so that it cannot compete with **IVa** micelles in the reactivity.

Thus the main factor responsible for the micelle effects of **IVa** (Δ) is the reactant concentration in the micelle phase, which in turn depends on the distribution coefficients P_S of the substrates: the greater the distribution coefficient, the greater the observed increase in the reaction rate (Tables 1, 2). The differences in the substrate distribution coefficients directly indicate how do the standard Gibbs energies ($\Delta G^0 = G_m^0 - G_{aq}^0 = -R T \ln P_S$) change in going from the aqueous to micelle phase. Transfer of substrates **I**–**III** to **IVa** micelles is accompanied by decrease in their Gibbs energies, and the maximal change of ΔG^0 (–5.0 kcal/mol) is observed for the most hydrophobic substrate **I** (see Table 1). Esters **I**–**III** are polar neutral organic compounds, and their solubility (see Experimental) increases in the series **I** < **II** ≈ **III**. Therefore, it is reasonable to presume that the main driving force of the reactant concentration effect is hydrophobic interactions responsible for substrate transfer.

The universal character of Eq. (17), which takes into account the effects of reactant concentration and change in the reactivity, allows us to compare the nucleophilicities of various functionalized surfactants: a necessary and sufficient condition is that the values of k_2, k_2^m, and K_S must be known. These requirements are met in the case of functionalized surfactants of the pyridinium series containing an oximate fragment, e.g., 1-alkyl-3-hydroxyiminomethylpyridinium halides which exhibit high reactivity toward phosphorus acid esters [9, 10, 22], including substrate **II**. The kinetic behavior of 1-dodecyl-3-hydroxyiminomethylpyridinium halide (**VI**), which at pH 9.3 gives rise to mixed micelles consisting of the cationic and zwitterionic surfactant species, in the reaction with ester **II** was

Table 1. Binding constants K_S and distribution coefficients P_S of *p*-nitrophenyl *p*-toluenesulfonate (**I**), diethyl *p*-nitrophenyl phosphate (**II**), and ethyl *p*-nitrophenyl ethylphosphonate (**III**) and second-order rate constants k_2 of the reactions of 1-methyl-3-(2-hydroxyiminopropyl)imidazolium (**Va**) and 1-cetyl-3-(2-hydroxyiminopropyl)imidazolium (**IVa**) halides with esters **I**–**III**; water, 25°C

Substrate no.	$k_2 \times 10^2$,[a] l mol^{-1} s^{-1}	$k_{OH} \times 10^3$, l mol^{-1} s^{-1}	$k_2^m \times 10^2$, l mol^{-1} s^{-1}	$k_m \times 10^2$, s^{-1}	K_S, l/mol l/mol	P_S,[b]	CMC $\times 10^4$,[c] M
I	1.5 ± 0.2	8.0 ± 0.3	3.0 ± 0.1	6.0 ± 0.06[d] 6.1 ± 0.4[e]	3300 ± 200[d] 3200 ± 100[f]	6500 ± 300 (–5.0)	0.540 ± 0.006
II	0.84 ± 0.06	9.6 ± 0.6	0.83 ± 0.02	1.65 ± 0.05[d] 1.6 ± 0.2[e]	280 ± 30[d] 270 ± 20[f]	550 ± 60 (–3.6)	2.4 ± 0.2 (S) 2.6 ± 0.4 (K)
III	9.0 ± 0.9	150 ± 10	16 ± 3	32 ± 3[d] 30 ± 5[e]	260 ± 20[d] 260 ± 10[f]	520 ± 50 (–3.5)	2.5 ± 0.2 (S)

[a] The pK_a value for compound **Va** is 10.70 ± 0.10 [23].

[b] The distribution coefficients P_S were calculated by the equation $K_S = P_S V_m$; in parentheses are given ΔG^0 values calculated by by the formula $\Delta G^0 = -RT\ln P_S$, kcal/mol, which characterize change in the standard Gibbs energy of the substrate in going from water to the micelle phase.

[c] Critical micelle concentrations were determined by the spectrophotometric (S) or kinetic (K) method.

[d] Calculated by Eq. (13).

[e] Calculated from k_{max} by Eq. (12).

[f] Calculated by Eq. (14).

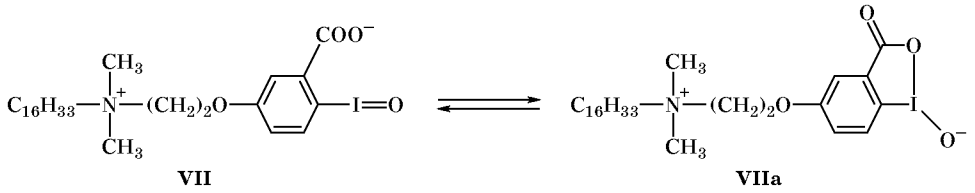
analyzed in terms of the pseudophase model, and the following kinetic and thermodynamic parameters were obtained: $k_2^m = 1.06 \times 10^{-2}$ l mol^{-1} s^{-1} and K_S = 56 l/mol [9]. Taking into account pK_a of the oximate fragment, the nucleophilic reactivity of **VI** toward ester **II** should be $k_2^m = 1.86 \times 10^{-2}$ l mol^{-1} s^{-1}. The corresponding value for the methyl analog, 1-methyl-3-hydroxyminomethylpyridinium iodide, estimated from the Brønsted relation for the reaction of oximate ions with ester **II** is $k_2 = 1 \times 10^{-2}$ l mol^{-1} s^{-1} [23]. Calculation of Δ for 1-methyl-3-hydroxyminomethylpyridinium iodide using Eq. (17) and assuming the fraction of bound substrate **II** to be $\alpha_S \ll 1$ and α_S = 0.1, 0.5, and 0.9 showed that the increase in the reaction rate in going from micelles of **VIa** to its methyl analog does not exceed a factor of 112, 100, 60, and 12, respectively; these values are considerably lesser than those found for surfactant **IVa** (Table 2).

One of the most active functionalized surfactants, which exhibit really catalytic properties in acyl group transfer reactions, is 5-[2-cetyl(dimethyl)ammonioethoxy]-2-iodosylbenzoate (**VII**) (Scheme 4) [19]. In aqueous solution of cetyl(trimethyl)ammonium chloride (**VIII**) compound **VII** exists mainly as heterocyclic tautomer **VIIa** which rapidly reacts with ester **II**, and the catalytic effect for the mixed micelle system **VIIa**–**VIII** is 43 600. However, the catalytic effect was estimated [19] with respect to 5-[2-cetyl-(dimethyl)ammonioethyl]-2-iodobenzoate rather than to the model analog of **VIIa**, heterocylcic tautomer of 2-iodosylbenzoate; also, neither binding constants nor k_2^m values were given, which are necessary for taking into account micelle effects by Eq. (17). Therefore, the kinetic data of [19] were treated by Eqs. (12) and (13)** to obtain $k_m = (3.7 \pm 0.1) \times 10^{-3}$ s^{-1}, $k_2^m = 1.85 \times 10^{-3}$ l mol^{-1} s^{-1}, and K_S = 320 ± 30 l/mol. Comparison of the K_S values (see also Table 1) indicates similar efficiencies in the solubilization of substrate **II** with micelles **IVa** and mixed micelles **VIIa**–**VIII**, while in both cases acceleration of the reaction due to effect of reactant concentration is the same (it cannot exceed $K_S/V_m = P_S$). Presumably, the same tendency is typical for the change of k_2^m/k_2*** in going to the micelle phase of **VIIa**, k_2^m/k_2(**VIIa**) ≈ 1 (cf. the corresponding k_2^m/k_2 value for **IVa**), and the maximal catalytic effect in the nucleophilic cleavage of ester **II** with functionalized **VIIa** micelles is unlikely to exceed Δ given in Table 2. It should be emphasized that the reactivity of **IVa** exceeds that of mixed **VIIa**–**VIII** micelles by a factor of 4, i.e., micelles

** The critical micelle concentration of compound **VIII** was reported in [34].

*** The value of $k_2 = 1.40 \times 10^{-3}$ l mol^{-1} s^{-1} for 2-iodosylbenzoate as a model of monomeric form of **VIIa** was estimated from the Brønsted relation for the reaction of inorganic α-nucleophiles with diethyl *p*-nitrophenyl phosphate (**II**) [35]; the value $k_2^m = 1.85 \times 10^{-3}$ l mol^{-1} s^{-1} was obtained on the basis of V_m = 0.5 l/mol [20].

Scheme 4.



VII **VIIa**

formed by zwitterionic surfactant **IVa** are more powerful nucleophilic species than mixed micelles formed by **VIIa** and **VIII**.

The above data unambiguously indicate that new functionalized surfactants **IV** are superior to previously known most powerful nucleophilic surfactants **VI** and **VII** [9, 10, 19, 22]. In fact, micelles formed by zwitterionic species **IVa** whose head part includes a covalently linked typical α-nucleophile moiety (oximate group) can be regarded as a unique supernucleophilic system ensuring high rates of substrate cleavage due to reactant concentration effect.

Table 2. Apparent rate constants for cleavage of *p*-nitrophenyl *p*-toluenesulfonate (**I**), diethyl *p*-nitrophenyl phosphate (**II**), and ethyl *p*-nitrophenyl ethylphosphonate (**III**) with 1-methyl-3-(2-hydroxyiminopropyl)imidazolium (**Va**) [k_{ap}(**Va**)] and 1-cetyl-3-(2-hydroxyiminopropyl)imidazolium (**IVa**) halides [k_{ap}(**IVa**)] and the corresponding values of $\Delta = k_{ap}$(**IVa**)/k_{ap}(**Va**); water, 25°C

Substrate no.	α_S[a]	k_{ap}(**IVa**) × 10^3,[b] s^{-1}	k_{ap}(**Va**) × 10^5,[c] s^{-1}	Δ[d]
I	–	–	–	13 200[e]
	0.035	2.11	0.0165	12 800
	0.107	6.53	0.054	12 100
	0.5	31	0.454	6800
	0.9	55	4.09 ± 0.08	1300
II	–	–	–	560[e]
	0.03	0.508	0.0928	550
	0.1	1.90	0.333	510
	0.5	8.30	3.0 ± 0.1	290
	0.9	14.9	25 ± 0.7	60
III	–	–	–	940[e]
	0.03	9.7	1.10 ± 0.08	900
	0.1	32	3.90 ± 0.09	820
	0.5	160	34.0 ± 0.6	460
	0.9	290	310 ± 9	94

[a] Fraction of the substrate bound with micelles of zwitterionic surfactant **IVa**.

[b] Corrected for the contribution of alkaline hydrolysis [Eq. (11)].

[c] The k_{ap}(**Va**) values given without standard deviations were calculated by Eq. (1), and the others were determined experimentally.

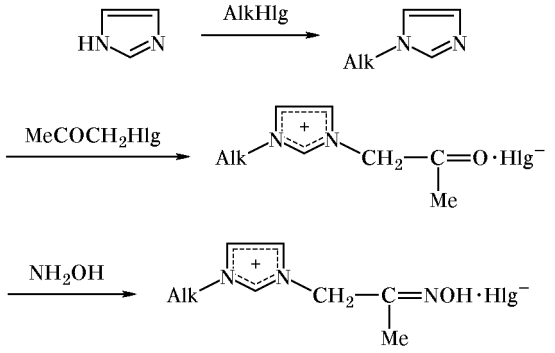
[d] Increase in the reaction rate in going from water to micelles of **IVa**.

[e] The highest possible acceleration $\Delta = (k_2^m/k_2)P_S$.

EXPERIMENTAL

p-Nitrophenyl *p*-toluenesulfonate, diethyl *p*-nitrophenyl phosphate, and ethyl *p*-nitrophenyl ethylphosphonate were synthesized by acylation of *p*-nitrophenol according to the procedure described in [30]. Commercial methyl iodide, cetyl bromide, and chloroacetone were purified by standard procedures; bromoacetone was prepared as described in [31]. 1-Methyl-3-(2-hydroxyiminopropyl)imidazolium halides and 1-cetyl-3-(2-hydroxyiminopropyl)imidazolium halides were synthesized according to Scheme 5, following the recommendations given in [32].

Scheme 5.



Initially, imidazole was alkylated with methyl iodide or cetyl bromide, and carbonyl group was then introduced into molecules of 1-alkylimidazoles via reaction with chloro- or bromoacetone. The resulting ketones were converted into the corresponding oximes by treatment with hydroxylamine in methanol [24]. After removal of the solvent, oximes **V** were recrystallized twice or thrice from butanol, and compounds **IV**, from ethanol–ether. Their melting points and ^{1}H NMR data are given below.

1-Methyl-3-(2-hydroxyiminopropyl)imidazolium halides. mp 165–168°C (bromide), 170–172°C

Table 3. Apparent pseudofirst-order rate constants k_{ap} for cleavage of *p*-nitrophenyl *p*-toluenesulfonate (**I**), diethyl *p*-nitrophenyl phosphate (**II**), and ethyl *p*-nitrophenyl ethylphosphonate (**III**) in the presence of 1-cetyl-3-(2-hydroxyiminopropyl)imidazolium bromide; water, 25°C

Ester **I**		Ester **II**		Ester **III**		Ester **I**		Ester **II**		Ester **III**	
$c_0 \times 10^4$, M	$k_{ap} \times 10^3$, s^{-1}	$c_0 \times 10^4$, M	$k_{ap} \times 10^3$, s^{-1}	$c_0 \times 10^4$, M	$k_{ap} \times 10^3$, s^{-1}	$c_0 \times 10^4$, M	$k_{ap} \times 10^3$, s^{-1}	$c_0 \times 10^4$, M	$k_{ap} \times 10^3$, s^{-1}	$c_0 \times 10^4$, M	$k_{ap} \times 10^3$, s^{-1}
0.04	0.63	0.2	0.78	0.313	5.92	2.1	21.6	83	12.1	300	280
0.08	0.695	0.9	0.85	0.625	6.1	2.5	25.5	110	12.8	350	290
0.1	0.815	1.8	0.95	1.35	6.1	3.57	31.0	150	13.8	400	290
0.117	0.82	2.0	1.04	2.6	6.8	4	32.4	210	14.4	500	300
0.15	1.13	3.6	1.28	3.28	12.4	4.2	33.5	300	15		
0.178	1.32	4.38	1.58	3.7	13.5	5.4	36.4	320	15.5		
0.20	1.33	5.0	1.9	4.52	21.9	6.4	38.6	400	15.4		
0.25	1.78	5.45	2	5.1	25	8.0	42.0	500	15.7		
0.32	2.0	6.0	2.22	5.84	31.4	10	44.8				
0.53	2.23	6.5	2.4	6.35	36	11	46.5				
0.65	2.73	7.5	3	6.8	37.2	16	49.9				
0.71	3.78	10.5	3.6	10	56	18	53.0				
0.806	5.53	15	4.6	12.6	69	24	54.5				
0.89	6.65	21	5.75	25	120	25	55.0				
0.90	7.14	25	6.8	41	170	27.8	55.0				
1.0	9.08	30	7.8	50	180	32	55.8				
1.05	9.15	33	8.5	75	210	50	57.8				
1.1	9.75	38	8.9	100	236	110	59.0				
1.25	11.7	41	9.5	135	250	160	59.0				
1.4	13.6	50	9.8	175	260	180	60.6				
1.8	18.7	58	10.5	200	270	210	61.0				
1.88	19	75	11.4	250	276						

(chloride). ^{1}H NMR spectrum, δ, ppm: 11.0 s (1H, NOH), 9.33 s (1H, 2-H, imidazole), 7.78 s and 7.70 s (2H, 4-H, 5-H, imidazole), 5.0 s (2H, NCH_2), 3.91 s (3H, NCH_3), 1.83 s (3H, CCH_3).

1-Cetyl-3-(2-hydroxyiminopropyl)imidazolium halides. mp 123–124°C (bromide), 125–127°C (chloride). ^{1}H NMR spectrum, δ, ppm: 11.15 s (1H, NOH), 9.55 s (1H, 2-H, imidazole), 7.85 s and 7.75 s (2H, 4-H, 5-H, imidazole), 5.05 s (2H, NCH_2), 4.25 t (2H, α-CH_2 in $C_{16}H_{33}$), 1.85 s (3H, CCH_3), 1.80 t (2H, β-CH_2 in $C_{16}H_{33}$), 1.25 m (26H, $C_{16}H_{33}$), 0.90 t (3H, ω-CH_3 in $C_{16}H_{33}$).

Inorganic reagents of ultrapure or chemically pure grade were used without additional purification. All solutions were prepared using doubly distilled water just before each series of kinetic measurements. The analytical concentration of oxime **V** was selected in such a way that the reactant solutions were simultaneously buffer solutions. The ionic strength was maintained with the aid of 1 M KCl. In solutions of **IV**, the ionic strength was not fixed. In all experiments, the required pH value was set using concentrated solutions of sodium hydroxide or hydrochloric acid. The acidity of the medium was checked before and after each kinetic experiment, using OP-205 and OP-213 pH-meters (Radelkis, Hungary). If the difference in pH before and after kinetic experiment exceeded 0.05 pH units, the results were rejected.

Nucleophilic cleavage of esters **I**–**III** by reagents **IVa** and **Va** in water at various pH values gives *p*-nitrophenoxide ion as one of the products (see Scheme 1); therefore, the progress of reactions was monitored following the accumulation of *p*-nitrophenoxide ion by spectrophotometry at λ 400–430 nm (Specord UV-Vis instrument, 25±0.5°C). The apparent pseudofirst-order rate constants k_{ap} (s^{-1}) were determined from the change in the optical density using Eq. (18):

$$\ln(D_\infty - D_\tau) = \ln(D_\infty - D_0) - k_{ap}\tau. \qquad (18)$$

Here, D_0, D_τ, and D_∞ are the optical densities at $\tau = 0$, $\tau = \tau_i$, and by the end of the process (Table 3). In all kinetic experiments the initial concentration of substrates **I**–**III** was much lesser than the initial nucleophile concentration.

The critical micelle concentrations (CMC) were determined by difference UV spectroscopy with the use of Fluorescein (λ 507 nm) [33] and from the kinetic data (Fig. 3a). The CMC value for the reaction of **IVa** with ester **I** was estimated by mathematical statistics [28]. The kinetic data (more than 40 values of k_{ap}) were treated according to Eq. (13) on variation of CMC ($c = c_0$ – CMC) in the range from 8×10^{-6} to 2×10^{-4} M through a step of 1×10^{-7} M; the linear correlation coefficient r was analyzed for statistical significance; a CMC value of 5.38×10^{-5} M was obtained. A similar value, 5.42×10^{-5} M, was obtained by treatment of nonlinear regression (11) by the quasi-Newton procedure at fixed $k_m = k_{max}$. The average CMC value, 5.40×10^{-5} M (Table 1) was used in the calculations of the kinetic and thermodynamic parameters.

The solubilities of esters **I**–**III** in water were determined as described in [9]: $\sim 1 \times 10^{-5}$ (**I**), $\sim 3 \times 10^{-3}$ M (**II** and **III**).

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