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## Supernucleophilic Systems Based on Functionalized Surfactants in the Decomposition of 4-Nitrophenyl Esters Derived from Phosphorus and Sulfur Acids. III.<sup>\*</sup> Reactivity of Mixed Micellar Systems Based on Tetraalkylammonium and Imidazolium Surfactants

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**Abstract**—Reactivity of mixed micellar systems based on the functionalized imidazolium and tetraalkylammonium surfactanats in the reaction of cleavage of 4-nitrophenyl ethyl ethylphosphonate was studied. Replacing of an imidazolium fragment in the detergent structure with a tetraalkylammonium one reveals decreasing the substrate solubilization efficiency. In the case of dimeric surfactants, the nucleophilicity of the oximate fragment is considerably (ca. 2 times) decreased thus additionally decreasing the rate of cleavage of the organophosphorus substarte. Therefore the nature of the cationic center in the head group may affect the extent of the observed micellar effects of functionalized surfactants.

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Solutions of surfactants are among the most favorable reaction media, in particular, for the nucleophilic cleavage of ester bonds [1-12]. They possess a unique combination of being environmentally friendly (since the main system component is water) [1-5], the possibility to ensure high reaction rates [1-9], and easily adjusting the properties by preparing multicomponent supramolecular ensembles (mixed micelles [10, 11], metallomicelles [12], surfactant–polymer aggregates [13-15], surfactant–calixarene [16, 17], etc.).

In the nucleophilic cleavage of esters of phosphorus and sulfur acids in micellar systems the best effect was observed at the use as cleavage agents of surfactants functionalized with the fragments of  $\alpha$ -nucleophiles [1–4, 8–10]. The obvious advantage of these detergents over the other types of micellar systems consists in the lack of the necessity to bind the reagent: its concentration is always maximal since the reactive fragment is covalently linked to the surfactant molecule [1, 2, 8, 9].

In the course of the last decade we have carried out a purposeful designing of monomeric and dimeric surfactants functionalized with an oxime group [1, 8, 9, 18-22]. A scientifically based designing of detergents possessing desired properties should be underlain by the establishment of the correlation between the structure and the micellar effects. The analysis of the correlation the structure of surfactant/ substrate-property made it possible to reveal the main factors governing the reactivity and the micellar effects of the functionalized surfactants. Thus, one of the key factors proved to be the nature of the head group since it to a large extent governs the structure, the surface charge, the partial molar volume of the micelle, the saturation of the micelle surface layer with water molecules, etc. [6–9]. In the most cases the  $\alpha$ nucleophilic functional moiety ensuring the nucleo-

<sup>\*</sup> For communication II, see [1].

philic cleavage of the acyl-containing substrates is also a part of the head group of the surfactant [1, 2, 8, 9, 18– 22]. Its reactivity, similar to that of the non-micelleforming structural analogs [8, 9, 19, 23, 24], is directly connected with its acid-base properties, and the Brønsted dependence has a break in the same  $pK_a$ range [1, 8, 9]. Beside the structure of the head group the micellar effects of the surfactant depend on the hydrophobic properties of substrate as well as of detergent [1, 8, 9, 18, 20–22]: with the growing length of the alkyl substituent in the surfactant and with the constant of the substrate binding the observed reaction rates increase.

Whereas the effect of the properties of the functional fragment, hydrophobicity of surfactant and substrate on the reactivity of the surfactant may be regarded as sufficiently clearly established [1, 8, 9, 18], the effect of the nature of the cationic center of the head group requires more detailed investigation.

In this study a method was developed of the synthesis of new functionalized tetraalkylammonium surfactants 1 and 2 and their micellar effect in the cleavage of 4-nitrophenyl ethyl ethylphosphonate 3 was estimated. The influence of detergents 1 and 2 on the rate of cleavage of ester 3 was compared with the micellar effects of their structural analogs, imidazole-containing surfactants 4 and 5, thus allowing the analysis of the influence on the reactivity of the nature of the cationic center.



The changes in the structure of the cationic center of dimeric surfactants 2 and 5 may result in more significant effect than in the case of monomeric detergents 1 and 4. This is due to the fact that micelles (and mixed micelles) of dimeric surfactants are considerably more sensitive to the structural changes in the surfactant [25].

Kinetic regularities of ester 3 cleavage with mixed micellar systems based on surfactant (1 and 2) and (4 and 5). Since the solubility of functionalized tetraalkylammonium detergents 1 and 2 turned out to be low, the quantitative estimation of the micellar effects and comparative analysis were performed using mixed micellar system functionalized surfactant–cetyltrimethylammonium bromide 6. In this approach the analysis of factors governing the observed acceleration may be properly performed considering the special features of the experimental conditions (fraction of functionalized detergent in the mixed micelles, ionization degree of the oxime fragment, etc.) [2, 7–10, 20].

The character of the influence of mixed micellar systems functionalized surfactant-6 on the rate of cleavage of substrate 3 is analogous to the laws previously established for micellar and mixed micellar systems based on surfactants containing in their structure of an oximate moiety [1, 8, 9, 18, 20-22]. Firstly, at the constant surfactant concentration the apparent reaction rate constant  $(k_{obs}, s^{-1})$  grows with increasing pH of the medium tending to a limit (Fig. 1). Consequently, the zwitter-ion forms of detergents 1 and 2 act as reactive forms, and the zwitter-ion is involved in a nucleophilic attack of the oximate-ion (Ox<sup>-</sup>) on the electron-deficient phosphorus atom leading to the formation of the corresponding *O*-acyl derivatives [2, 8, 26, 27]. Secondly, the dependences of  $k_{obs}$  on the summary concentration of the surfactant  $(c_0, \text{ mol } L^{-1})$  at pH = const have the pattern typical of the ester cleavage in the presence of functionalized detergents [1, 8, 9, 18, 20 - 22]: till the critical micelle concentration (CMC, mol  $L^{-1}$ ) only a slight acceleration is observed, and then with the growing concentration of micellized surfactant ( $c = c_0 - CMC$ , mol  $L^{-1}$ ) the  $k_{obs}$  values significantly increase due to the growing binding of the substrate with micelles (mixed micelles) of the surfactant (Figs. 2, 3).

The analysis of kinetic data (like those of previously studied functionalized detergents and mixed micellar systems based thereon) was performed in the frame of the pseudophase distribution model [1, 2, 7, 9, 20, 28]. Therewith it is assumed that the cleavage of ester **3** in the presence of mixed micelles proceeds along two parallel routes:

In the scheme the designations OxH, Ox<sup>-</sup> correspond to the functionalized detergents with the non-ionized and ionized functional groups,  $P_{\rm S} = [S]_{\rm m}/[S]_{\rm w}$  is the distribution coefficient of the substrate (S) between two phases, micellar pseudophase (m) and water (w);  $k_2^{\rm m}$  and  $k_{\rm OH}^{\rm w}$  L mol<sup>-1</sup> s<sup>-1</sup>, are the second order rate constants characterizing the nucleophilicity of the oximate group in the micelles of the surfactant and OH<sup>-</sup> ion in water. The apparent rate constant of the pseudofirst order is described by the Eq. (1):

$$k_{\rm app.} = \frac{\chi \cdot k^{\rm m} K_{\rm S} C + k_{\rm OH}^{\rm w} \cdot a_{\rm OH}^{\rm -}}{1 + K_{\rm S} C} \cdot \frac{K_{\rm a, app}}{K_{\rm a, app} + a_{\rm H}^{\rm +}}$$
$$= \frac{\chi (k_2^{\rm m} / V_{\rm m}) K_{\rm S} c + k_{\rm OH}^{\rm w} \cdot a_{\rm OH}^{\rm -}}{1 + K_{\rm S} c} \cdot \frac{K_{\rm a, app}}{K_{\rm a, app} + a_{\rm H}^{\rm +}}, \quad (1)$$

where  $\chi$  is the molar fraction of the functionalized detergent in the mixed micelle;  $k^{\rm m}$ , s<sup>-1</sup>, is the reduced nucleophilic reactivity of the functional fragment in the micellar pseudophase;  $K_{\rm S} = (P_{\rm S} - 1)V_{\rm m} \approx P_{\rm S}V_{\rm m}$ , L mol<sup>-1</sup>, is the constant of the equilibrium binding of



Fig. 1. Dependence of the rate of substrate 3 cleavage in a mixed micellar system 2/6 on pH of environment;  $\chi 0.25$ ,  $c_0 0.0158$  mol L<sup>-1</sup>, borate buffer solution 0.01 mol L<sup>-1</sup>, 25°C.

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**Fig. 2.** Concentration dependences for substrate **3** cleavage in mixed micellar systems 1/6,  $\chi$  0.25 (*1*) and 2/6,  $\chi$  0.25 (*2*); pH 10.5, borate buffer solution 0.01 mol L<sup>-1</sup>, 25°C.



Fig. 3. Concentration dependences for substrate 3 cleavage in mixed micellar system 1/6:  $\chi 0.25$  (1),  $\chi 0.125$  (2); pH 10.5, borate buffer solution 0.01 mol L<sup>-1</sup>, 25°C.

the substrate;  $V_m$ , L mol<sup>-1</sup>, is the partial molar volume of the surfactant; c, mol L<sup>-1</sup>, is the concentration of the micellized detergent;  $K_{a,app}$  is the apparent constant of acid ionization of the oxime group.

When estimating the kinetic parameters from Eq. (1) the contributions from the alkaline hydrolysis in the micellar pseudophase and the cleavage of substrate **3** by the functional group of non-micellized part of the surfactant in the water phase were not taken into account since under the chosen experimental conditions their rates are low and did not essentially contribute to the  $k_{obs}$  value.

All concentration and pH-dependences are adequately described in the framework of the above

**Table 1.** Physicochemical properties and nucleophilic reactivity of detergents 1, 2, 4, and 5 in the cleavage of ester 3; borate buffer solution 0.01 mol  $L^{-1}$ , 25°C<sup>a</sup>

Compound no.	$pK_a^b$	γ <sup>c</sup>	pН	$\alpha^{d}$	$k_{2}^{\rm m}/V_{\rm m}$ , s <sup>-1</sup>	$k_{2}^{m}$ , L mol <sup>-1</sup> s <sup>-1e</sup>	$K_{\rm S}$ , L mol <sup>-1</sup>	CMC, mol L <sup>-1f</sup>
1	10.15 (sp, χ 1.0) 10.23 (sp, χ 0.125)	0.25 0.25	11.30 10.45	~ 0.9 ~ 0.5	0.33	0.13 0.13	70 70	0.001 0.002
		0.125	10.48	~ 0.5	0.33	0.13	60	0.0006
2	9.44 (sp, χ 1.0) 9.21 (kin, χ 0.25) 9.49 (sp, χ 0.125)	0.5 0.25 0.25	10.45 10.46	$\sim 0.9$ $\sim 0.9$ 0.1 1.0 <sup>g</sup>	0.19 0.20 $0.20^{g}$	0.076 0.080 0.080 <sup>g</sup>	72 74 74	0.0004 0.0003
		0.23	10.46	~ 0.9	0.19	0.080	93	0.0003
4	10.50 (sp, χ 1.0) 10.10 (kin, χ 1.0) 10.29 (sp, χ 0.125)	1.0 1.0 0.5	11.40 10.32 11.50	$\sim 0.9$ $\sim 0.5$ $\sim 0.9$	0.21 0.28 0.30	0.11 0.14 0.12	70 76 95	0.003 0.0035 0.0006
		0.5 0.125	10.43 11.43	$\sim 0.5$ $\sim 0.9$	0.30 0.33	0.12 0.13	91 162	0.0006 0.0004
		0.125	10.53	~ 0.5	0.28	0.11	155	0.0006
5	8.8 (kin, χ 1.0) 8.9 (sp, χ 1.0) 8.9 (sp, χ 0.125)	1.0 0.125	10.00 10.51	~0.9 >0.9	0.40 0.43	0.20 0.17	155 160	0.00005 0.0001
	1		1			1	1	1

<sup>a</sup> The determination error of values  $k_{m}^{m}/V_{m}$  from kinetic data did not exceed ±10%, of  $K_{s}$  and CMC was no larger than ±15%. Data for surfactants 4 and 5 at  $\chi$  1.0 are taken from [1, 18].

<sup>b</sup> Values of  $pK_a$  were determined from kinetic (kin) or spectrophotometric (sp) data.

<sup>c</sup> Molar fraction of functionalized detergent in mixed micelles with compound **6**.

<sup>d</sup> Fraction of anionic form of the oxime fragment of surfactant.

<sup>e</sup> In calculation of  $k_2^m$  values at  $\chi$  1.0 the partial molar volume was assumed at 0.5 01 mol L<sup>-1</sup> [1, 9, 12, 21], and that of mixed micelles ( $\chi$  0.125–0.5) was assumed as equal to the partial molar volume of detergent **6**, ~0.4 01 mol L<sup>-1</sup> [6, 7].

<sup>f</sup> CMC values were calculated from kinetic data.

<sup>g</sup> Parameters were obtained by processing the dependence  $k_{obs}$ -pH.

model [Eq. (1)]. In Table 1 the values of  $pK_{a,app}$ ,  $k_2^m$  and the other parameters of the systems based on surfactants 1, 2 and 4, 5 are compiled, characterizing the cleavage of ester 3 with these compounds in the micellar pseudophase. The CMC values were estimated from kinetic data (Fig. 4).

Acid-base properties and the nucleophilicity of surfactants (1 and 2) and (4 and 5). The apparent constants of acid ionization of the oxime group in detergents 1, 2, 4, and 5 and in mixed micellar systems functionalized surfactant–6 were determined by spectrophotometry and/or by kinetic method (Table 1). The character of changes in  $pK_{a,app}$  of the oxime group is of the same type in the surfactants with a different nature of the cationic center: Regardless of its structure in going from of monomeric to dimeric surfactants the acidity of the oxime fragment increases in agreement with the influence of the second electron-acceptor substituent (cf.  $pK_{a,app}$  of these changes are different:

 $pK_{a,app}$  of compound **2** relative  $pK_{a,app}$  **1** decreases by ~0.8 log unit, and  $pK_{a,app}$  of compound **5** relative to **4** diminishes by ~1.5 log unit. The variation of the



Fig. 4. Determination of CMC by the kinetic method for the mixed micellar system 2/6; substrate 3,  $\chi$  0.5, pH 10.5, borate buffer solution 0.01 mol L<sup>-1</sup>, 25°C.



Fig. 5. Brønsted dependence for substrate 3 cleavage with functionalized surfactants containing an oxime group (points for surfactants 1, 2, 4, and 5, all others are taken from [1, 9, 19, 20]).

fraction of the functionalized detergent does not considerably affect the values of  $pK_{a,app}$ , although it was presumed that the increasing content of the cationic detergent **6** in the mixed micelles with **1**, **2** and **4**, **5** should favor the ionization of the oxime group due to the growing contribution of the field effect [6, 22].

The analysis of the kinetic behavior of surfactants 1, 2 and 4, 5 in the frame of the pseudophase distribution model allows the establishment of the following laws in the changes of the nucleophilicity of the oximate group. Firstly, according to the level of the nucleophilicity the studied surfactants form the following series:  $k_2^{m}(5) > k_2^{m}(4) \approx k_2^{m}(1) > k_2^{m}(2)$  (Table 1). Secondly, the reactivity of the oximate fragment is independent of the fraction of the functionalized detergent in the mixed micelles  $(k_2^m, \text{ Table 1})$ . Since the character of microsurrounding is one of the main factors affecting the  $k_2^m$  value at the variation of the composition of mixed micelles [1, 6, 7, 22] the constancy of this value shows the relatively constant properties of the surface layer and its close properties to those of the micelles 6. Thirdly, whereas for the monomeric (1 and 4) and dimeric surfactant 5 the nucleophilicity of the oximate group corresponds to the Brønsted dependence for the functionalized detergent, the point of dimeric surfactant 2 shows a significant negative deviation (Fig. 5). It is apparently due to the higher conformational mobility of the head group in detergent 2 than in surfactant 5 [25, 29]. This provides a possibility for an efficient electrostatic interaction between the negatively charged oxygen

atom of the oximate group and the positively charged nitrogen atom of the tetraalkylammonium fragment resulting in the reduction of the nucleophilic reactivity.

effects of systems Micellar based on functionalized surfactants (1 and 2) and (4 and 5) in the cleavage of ester 3. The values of apparent micellar effects for the system based on functionalized surfactants in the cleavage of ester 3 may be characterized by the ratio of the apparent rate constants at the constant pH, initial concentration and the value of  $\chi$ . At the detergent concentration in micelles exceeding ~10-fold the CMC and at similar experimental conditions the maximum increase in  $k_{obs}$  is observed for the mixed micelles of detergent 5: approximately 3–4-fold compared with monomeric (1 and 4) and dimeric (2) surfactants [Table 2,  $k_{obs}^{m}(5)/k_{obs}^{m}(sur$ factant)]. Even more significant differences are observed at the comparison of the apparent rate constants in the micellar pseudophase and in water.<sup>\*</sup> In this case the reaction rate grows 200-500 times (Table 2).

With the growing fraction of the functionalized detergent in the mixed micelles with surfactant **6** the values of  $k_{obs}$  regularly grow (Fig. 3) and consequently the half-time of substrate conversion into the reaction products considerably decreases. For instance, for the mixed micelles **2**/**6** at pH 10.5,  $c_0$  0.0029 mol L<sup>-1</sup>,  $\chi$  0.125,  $\tau_{1/2}$  attains about 180 s, and at  $\chi$  0.5  $\tau_{1/2}$ , ~50 s.

Influence of structural factors on micellar effects of monomeric (1 and 4) and dimeric (2 and 5) surfactants in the cleavage of ester (3). Micellar effects of monomeric and dimeric detergents in the cleavage of acyl-containing substrates depend on quite a number of factors: concentrating reagents in micelles (mixed micelles), changes in the reactivity of the functional group, ester orientation in the micellar pseudophase, the shift in the apparent constants of acid ionization, etc. [1, 2, 8, 9, 18, 20-22]. The importance of each factor depends significantly on noncovalent interactions, first of all, hydrophobic ones, which are directly connected with the hydrophobicity of the substrate and the surfactant [1, 9, 18, 21, 22]. The analysis of kinetic data allows establishing the following. Firstly, at pH = const the micellar effects depend on the acidity of the oxime group of the detergent: The lower its value, the higher is the

<sup>\*</sup> The  $k_{obs}$  in water were estimated from the second order rate constants of the non-micelle-forming oximes possessing p $K_a$ , comparable with the basicity of the functional group of detergents **1**, **2**, **4**, and **5** [1, 9, 19, 20].

	e e	<i>, ,</i> ,	, <b>1</b>			
Surfactant	$CMC \cdot 10^4$ , mol $L^{-1}$	$\alpha^{a}$	$c_0 \cdot 10^3$ , mol L <sup>-1b</sup>	$k_{\rm obs} \cdot 10^3$ , s <sup>-1</sup>	$k_{\rm obs}^{\rm m}(5)/k_{\rm obs}^{\rm m}({\rm surfactant})^{\rm c}$	$k_{\rm obs}^{\rm m}/k_{\rm obs}^{\rm w}{}^{\rm d}$
1	6.0	~0.5	2.7	2.5	~ 4.4	~ 230
2	3.0	1.0	2.7	3.9	~ 2.8	~ 180
4	4.0	~0.5	2.3	3.6	~ 3.0	~ 330
5	1.0	1.0	2.4	10.9	1.0	~ 500

**Table 2.** Micellar effects of mixed micellar systems based on imidazolium and tetraalkylammonium functionalized surfactants in the cleavage of ester **3**;  $\chi$  0.125, pH 10.5, borate buffer solution 0.01 mol L<sup>-1</sup>, 25°C

<sup>a</sup> Ionization degree of the functional fragment.

<sup>b</sup> Summary concentration of the surfactant.

<sup>c</sup> Ratio of apparent rate constants of surfactant 5 to  $k_{obs}(1)$ ,  $k_{obs}(2)$ ,  $k_{obs}(4)$ .

<sup>d</sup> Ratio of values  $k_{obs}^{m}$  to the apparent rate constants of substrate **3** cleavage with anions of non-micelle-forming oximes in water ( $k_{obs}^{w}$ ). The data on non-micelle-forming oximes are taken from [1, 9, 19, 20].

concentration of the nucleophilic fragment. Near pH  $\sim 10.5$  monomeric detergents 1 and 4, as also the dimeric surfactant 2, react with substrate 3 with approximately equal rates, and the maximum values of  $k_{\rm obs}$  are found for compound 5 (Figs. 6, 2). However the fractions of ionized nucleophilic group of the surfactant in these conditions are different:  $\alpha(1) \approx \alpha(4)$  $\approx 0.5$ ,  $\alpha(2) \approx \alpha(5) \approx 1.0$ . With accounting for the fraction of the ionized functional fragment  $\left[\alpha = K_{a,app}\right]$  $(K_{a,app} + \alpha_{H})$  the sequence of the variation of the apparent rate constants of the reaction is another (Fig. 7): at  $c_0 = \text{const } k_{obs}/\alpha$  5 > 4 > 1 > 2. Secondly, the character of variation in  $k_{obs}$  and  $k_{obs}/\alpha$  reflects not only the difference in the concentration of the oximate fragment (because of different ionization degree of the surfactant), but also the existing distinctions in the reactivity (Figs. 6, 7). The value  $k_2^m/V_m$  for detergent 2



Finally, just the effects of reagents concentrating govern the increase in the reaction rate at the transition of the process in the micellar pseudophase [1, 6, 7, 9, 18, 20, 21]. The efficiency of substrate solubilization is characterized by the corresponding binding constants ( $K_S$ , Table 1). Under the identical experimental condition (at the fraction of functionalized detergent  $\chi$ 0.125 in the mixed micelles with compound **6** and pH 10.5)  $K_S(\mathbf{5}) \approx K_S(\mathbf{4}) > K_S(\mathbf{2}) > K_S(\mathbf{1})$ . Considering the character of the change in the nucleophilicity of the functional fragment of the surfactant [ $k_2^m(\mathbf{5}) > k_2^m(\mathbf{4}) \approx$  $k_2^m(\mathbf{1}) > k_2^m(\mathbf{2})$ ] and the efficiency of the substrate binding [ $K_S(\mathbf{5}) \approx K_S(\mathbf{4}) > K_S(\mathbf{2}) > K_S(\mathbf{1})$ ] the decrease in



**Fig. 6.** Dependences of apparent rate constants ( $k_{obs}$ , s<sup>-1</sup>) of substrate **3** cleavage on the concentration of functionalized surfactants **1**, **2**, **4**, and **5**;  $\chi$  0.125, pH 10.5, borate buffer solution 0.01 mol L<sup>-1</sup>, 25°C.



**Fig. 7.** Dependences of  $k_{obs}/\alpha$  values on the concentration of functionalized surfactants **1**, **2**, **4**, and **5** for the substrate **3** cleavage;  $\chi 0.125$ , pH 10.5, borate buffer solution 0.01 mol L<sup>-1</sup>, 25°C ( $\alpha$  is the degree of ionization of the functional group).

Cetyltrimethylammonium bromide 6 purchased from Sigma Aldrich (BioUltra,  $\geq$  99.0%) and inorganic reagents of grades "pure for analysis" and "extrapure" were used without additional purification. The solutions were prepared in bidistilled water.

All solutions were prepared just before the kinetic

measurements. The required pH values were obtained

adjusting at 25°C by adding small portions of conc.

KOH. The pH was measured with pH-meter Metrohm

744. The reaction progress was monitored by spectro-

photometry following the accumulation of 4-nitrophe-

nolate ion (water, 25°C, 400-410 nm; spectrophoto-

meter Genesys 10 S UV-VIS, Thermo Electron Corp).

The method of calculation of the apparent rate constants

of the pseudofirst order ( $k_{obs}$ , s<sup>-1</sup>), the detailed description of the procedure of the kinetic experiment, and the

method of the spectrophotometric determination of  $pK_a$ 

4 and 5 was described in [1, 18]. 4-Nitrophenyl ethyl ethylphosphonate 3 was obtained and purified by procedure [20].

**EXPERIMENTAL** Synthesis of functionalized imidazolium surfactants

for the tetraalkylammonium fragment results in decrease in the observed micellar effects therefore in designing new supernucleophilic systems it is more feasible to use the functionalized imidazolium surfactants.

based on tetraalkylammonium surfactants 1 and 2

appear as unexpected and require more detailed

investigation since under given conditions (at  $\gamma$  0.125)

the properties of mixed micelles 1/6 and 2/6 should be materially identical to the properties of individual

micelles 6, where  $K_{\rm S}$  of ester 3 lies in the range 160– 250 L mol<sup>-1</sup> (as is observed for the mixed micelles

based on imidazolium surfactants 4 and 5 [9, 20] and

designing supernucleophilic systems the changes in the

structure of the cationic center of the head group of the

functionalized surfactant also may affect its properties,

and the strongest effect would be observed in dimeric

detergents. The replacement of the imidazolium core

Therefore the results obtained show that in

the other similar systems [22]).

is expectable.

the micellar effects in the series 5 > 4 > 1 > 2 (Fig. 7) <sup>1</sup>H NMR spectra were registered on a spectrometer Bruker Avance II-400 (400 MHz) in DMSO- $d_{6}$ , internal reference TMS. Relatively low  $K_{\rm S}$  values for mixed micellar system

> 1-Chloroacetoxime was synthesized by procedure [30]. Yield 52%, bp 52–54°C (0.75 mmHg). <sup>1</sup>H NMR spectrum, δ, ppm: 1.83 s (3H, CH<sub>3</sub>), 4.22 s (2H, CH<sub>2</sub>), 11.07 s (1H, NOH). Found, %: C 33.02; H 5.67; Cl 33.10; N 13.50. C<sub>3</sub>H<sub>6</sub>CINO. Calculated, %: C 33.51; H5.62; Cl 32.97; N 13.03.

> [2-(Hydroxyimino)propyl]dimethylamine. Α mixture of solutions of 10 g (0.09 mol) of 1chloroacetoxime in 20 mL of ethanol and 50 mL of 40% aqueous dimethylamine was heated for 24 h in a hermetically sealed vessel at 60°C. On cooling the reaction mixture was tice extracted with ethyl ether. Combined ether extracts were dried with sodium sulfate, evaporated, the residue was crystallized from methanol. Yield 6.2 g (57%), mp 98–99°C. <sup>1</sup>H NMR spectrum, δ, ppm: 1.74 s (3H, CH<sub>3</sub>), 2.09 s (6H, 2CH<sub>3</sub>), 2.83 s (2H, CH<sub>2</sub>), 10.50 s (1H, NOH). Found, %: C 52.07; H 10.87; N 23.94. C<sub>5</sub>H<sub>12</sub>N<sub>2</sub>O. Calculated, %: C.70; H 10.41; N 24.12.

> [2-(Hydroxyimino)propyl]dimethyldodecylam**monium bromide (1)**. To a solution of 1 g (9 mmol) of [2-(hydroxyimino)propyl]dimethylamine in 20 mL of ethanol at room temperature was added by portions an emulsion of 2.14 g (9 mmol) of dodecyl bromide in 20 mL of ethanol. The mixture was heated for 48 h in a hermetically sealed vessel at 65°C, then it was evaporated on a rotary evaporator. The residue was crystallized from acetone. Yield 0.75 g (24%), mp 104–106°C. <sup>1</sup>H NMR spectrum, δ, ppm: 0.85 t (3H, CH<sub>3</sub>, J 6.7 Hz), 1.19–1.33 m [18H, (CH<sub>2</sub>)<sub>9</sub>], 1.65–1.75 m (2H, CH<sub>2</sub>), 1.96 s (3H, CH<sub>3</sub>), 3.03 s (6H, 2CH<sub>3</sub>), 3.24-3.30 m (2H, CH<sub>2</sub>N<sup>+</sup>), 4.07 s (2H, CH<sub>2</sub>N<sup>+</sup>), 11.77 ms (1H, NOH). Found, %: C 56.10; H 10.77; Br 21.51; N 7.39. C<sub>17</sub>H<sub>37</sub>BrN<sub>2</sub>O. Calculated, %: C 55.88; H 10.21; Br 21.87; N 7.67.

> 1,3-Dichloroacetoxime was synthesized by procedure [31]. Yield 54%, bp 100–105°C (0.75 mmHg). <sup>1</sup>H NMR spectrum, δ, ppm: 4.35 s (2H, CH<sub>2</sub>), 4.38 s (2H, CH<sub>2</sub>), 12.00 s (1H, NOH). Found, %: C 25.25; H 3.37; Cl 49.21; N 9.74. C<sub>3</sub>H<sub>5</sub>Cl<sub>2</sub>NO. Calculated, %: C 25.38; H 3.55; Cl 49.94; N 9.86.

> $N^{1}$ ,  $N^{3}$ -Didodecyl-2-(hydroxyimino)- $N^{1}$ ,  $N^{1}$ ,  $N^{3}$ ,  $N^{3}$ tetramethylpropane-1,3-diammonium chloride (2). A mixture of 0.27 g (1.9 mmol) of 1,3-dichloroacetoxime, 0.8 g (3.8 mmol) of N,N-dimethyldodecyl

amine (Sigma Aldrich, 97%), and 10 mL of anhydrous ethanol was heated for 48 h in a hermetically sealed vessel at 90°C. On cooling the precipitated crystals were filtered off and washed with a minimal quantity of anhydrous ethanol. Yield 0.75 g (70%), mp 142– 144°C. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.85 t (6H, 2CH<sub>3</sub>, *J* 6.7 Hz), 1.25 m [36H, 2(CH<sub>2</sub>)<sub>9</sub>], 1.67–1.77 m (4H, 2CH<sub>2</sub>), 3.09 s (12H, 4CH<sub>3</sub>), 3.31–3.40 m (4H, 2CH<sub>2</sub>N<sup>+</sup>), 4.29 s (2H, CH<sub>2</sub>N<sup>+</sup>), 4.35 s (2H, CH<sub>2</sub>N<sup>+</sup>), 13.52 s (1H, NOH). Found, %: C.35; H 11.68; Cl 12.58; N 7.45. C<sub>31</sub>H<sub>67</sub>Cl<sub>2</sub>N<sub>3</sub>O. Calculated, %: C 65.46; H11.87; Cl 12.46; N7.39.

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