Supramolecular catalytic systems based on 1,4-diazabicyclo[2.2.2]octane, its alkylated quaternary derivatives, and lanthanum nitrate*

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Spectrophotometry was used to study the catalytic effects of the systems composed of *N*-mono- and *N*,*N*-dialkylated 1,4-diazabicyclo[2.2.2]octanes and lanthanum nitrate on the hydrolysis rate of *O*-alkyl *O*-4-nitrophenyl chloromethylphosphonates (Alk = Et, Bu^n, and *n*-hexyl). The mechanism of action and efficiency of the catalytic system depend on the structure of the heterocycle, its propensity to aggregation and complexation with the lanthanum cation, and the relative content of the components in solution. The maximum catalytic effect (a ~115-fold increase in the hydrolysis rate constant) was achieved in micellar solutions of the cationic monoalkylated derivative of 1,4-diazabicyclo[2.2.2]octane and lanthanum nitrate.

Key words: 1,4-diazabicyclo[2.2.2]octane, *N*-mono- and *N*,*N*-dialkylated 1,4-diazabicyclo[2.2.2]octanes, catalysis, hydrolysis, phosphorus acid esters.

The effect of supramolecular (including micellar) systems containing amphiphilic compounds on chemical reactions is an attractive subject of investigations. The use of such systems allows one to regulate the rate and mechanism of reactions and carry out the processes in various (both aqueous and nonaqueous) media under mild conditions. In addition, such catalytic systems can be highly effective even in low concentrations, which meets the green chemistry requirements.[1—3] The biomimetic character of supramolecular systems is also of great importance.[4—6]

The catalytic effect of micellar solutions of surfactants can be enhanced, *e.g.*, by using metallomicelles (aggregates formed by metal—ligand complexes). For instance, the hydrolysis of carboxylic and phosphorus acid esters is crucial in biochemical transformations and decomposition of poisoning substances and ecotoxicants. The acceleration of these processes by metallomicelles is due to simultaneous electrophilic and micellar catalysis initiated by coordination of the substrate to the metal. This coordination gives rise to the formation of a ternary metal—ligand—substrate complex followed by a nucleophilic attack of a metal-bound hydroxide ion on the substrate.[7,8]

To understand the complex mechanism of action of metallomicellar systems, it is important to elucidate the contributions from different types of catalysis to the resultant catalytic effect and assess the possibility of the synergism. The goal of the present work was to design novel catalytic systems based on *N*-mono- (MAD) and *N*,*N*-dialkylated (DAD) derivatives of 1,4-diazabicyclo-[2.2.2]octane (DABCO) and a La^{3+} salt; MAD and DAD are micelle-forming cationic surfactants containing a bicyclic head group. Such systems can be assumed to control the rate of hydrolytic P—O(ester) cleavage. For comparison, we studied the catalytic properties of DABCO and the DABCO—La^{3+} system. A specific feature of the systems under study is that MAD and DAD can act as micellar catalysts, while DABCO (a tertiary diamine) plays the part of a basic catalyst for nucleophilic substitution reactions of phosphorus acid esters.[9—11] In addition, DABCO and MAD, which are both electron donors, can form complexes with transition metal cations in aqueous, water—alcohol, and nonaqueous media,[12—15] thus enabling the formation of catalytically active metal complexes and metallomicelles. Lanthanum nitrate was chosen because of a reported[8,16] additional catalytic effect possibly produced by La^{3+} ions (*via* electrophilic catalysis) on nucleophilic substitution reactions of phosphorus acid esters.[8,16] Although La^{3+} complexes with N-donating ligands are less stable than those with O-donors, lanthanum nitrate form stable complexes with various linear[17] and cyclic[18] amines, the other ligands being the nitro group and water. The complexes in the systems under consideration seem to have the same compositions as their analogs with O-donors. Earlier, we have obtained a stable (in aqueous media) complex from hexadecyl MAD and lanthanum nitrate (surfactant : La^{3+} = 2 : 1), thus providing evidence of the stability of such complexes.

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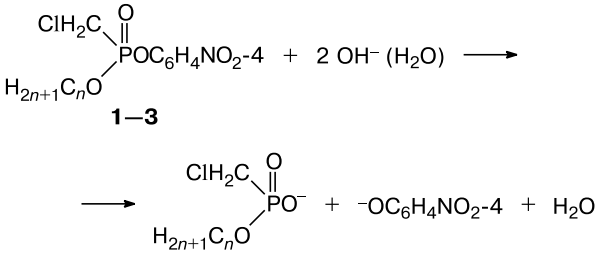
One can assume that a study of catalytic activity in the series DABCO, MAD, and DAD in the presence of lanthanum cations will be useful for estimation of the efficiency some or other type of catalysis. It is worth noting that DABCO, its alkylated derivatives, and metal complexes with DABCO are among the compounds that attract an increased attention of researchers. Such compounds have strong antibacterial and antifungal effects[19—21] and find use as ion-exchange materials in chromatography,[22] antioxidants,[23,24] components of ionic liquids,[25] catalysts for the Suzuki—Miyaura, Sonogashira, and Heck cross-coupling reactions[26—29] as well as for the Baylis—Hillman reaction[30] and alcohol oxidation.[31]

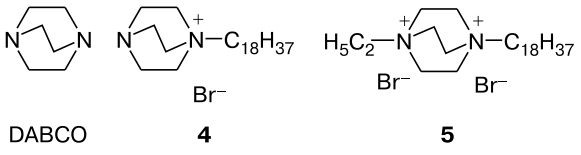
Earlier, we have revealed a high aggregation tendency of 1-alkyl-4-aza-1-azoniabicyclo[2.2.2]octane bromides and 1-alkyl-4-ethyl-1,4-diazoniabicyclo[2.2.2]octane dibromides (Alk = n-C_nH_{2n+1}, n = 12, 14, 16, and 18) and their catalytic activity in the hydrolysis of phosphorus acid esters.[19,32—36] In the present work, we studied the basic hydrolysis of *O*-alkyl *O*-4-nitrophenyl chloromethylphosphonates (**1**—**3**) as a model process (Scheme 1).

Scheme 1



n = 2 (**1**), 4 (**2**), 6 (**3**)

DABCO, 1-octadecyl-4-aza-1-azoniabicyclo[2.2.2]-octane bromide (**4**), 1-ethyl-4-octadecyl-1,4-diazoniabicyclo[2.2.2]octane dibromide (**5**), and lanthanum nitrate hexahydrate were used as components of the catalytic system. Basic hydrolysis was carried out in aqueous 0.001 *M* NaOH.



Experimental

DABCO (98% purity) and $La(NO_3)_3 \cdot 6H_2O$ (99% purity) (Sigma-Aldrich) were employed as purchased. Monocationic surfactant **4** was prepared from DABCO and 1-bromooctadecane as described earlier.[32] Dicationic surfactant **5** was prepared by quaternization[19] of compound **4** with 1-bromoethane. Substrates **1**—**3** were synthesized according to a known procedure.[37,38]

The hydrolysis kinetics was studied by spectrophotometry while monitoring the increasing optical density of the absorption band of the 4-nitrophenolate anion (λ_{max} = 400 nm). Electronic absorption spectra were recorded on a Specord UV-Vis spectrophotometer (Germany) in temperature-controlled cells. The apparent rate constants k_{app} were calculated under the assumption that the reaction rate obeys a first-order equation. The difference between the k_{app} values obtained in parallel measurements did not exceed 5%. The initial concentration of phosphonates **1**—**3** was $5 \cdot 10^{-5}$—$1 \cdot 10^{-4}$ mol L^{-1}; pH was measured with a pH-211 ionometer (Russia). All solutions of interest were prepared from twice-distilled water.

Results and Discussion

The catalytic effect of the system under study depends on its composition. In individual solutions of DABCO, its alkylated derivatives **4** and **5**, and lanthanum nitrate, the increased hydrolysis rates are caused by basic, micellar, and electrophilic catalysis, respectively.

In the case of DABCO, the first-order rate constant k_{app} is a linear function of its concentration C_{DABCO} (Fig. 1) that obeys the equation

$$k_{app} = A + BC_{DABCO}, \quad (1)$$

where A and B are the constants specified in Table 1.

For the concentration range studied, the catalytic effect of DABCO provides a 2.3- and 2.6-fold increase in the rate constant for phosphonates **1** and **3**, respectively.

When studying individual solutions of compounds **4** and **5** (0.001 *M* NaOH, 25 °C), we have demonstrated[34,35] that the concentration dependences of k_{app} are shaped like those characteristic of micelle-catalyzed processes and are described by curves with maxima. The rate constant of the basic hydrolysis of compound **2** in the presence of derivatives **4** and **5** increases by factors of 74 and 33, respectively.

The presence of lanthanum nitrate also catalyzes the hydrolytic P—O(ester) cleavage. The hydrolysis of the

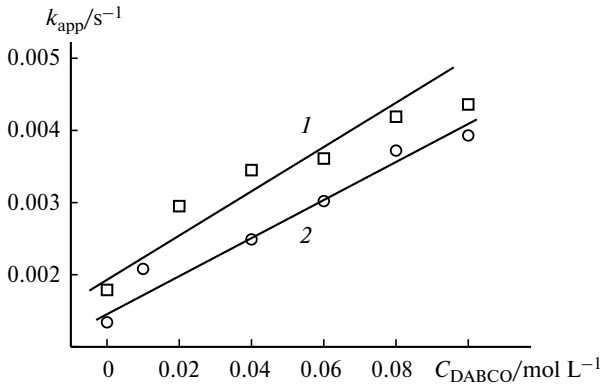


Fig. 1. Plots of the apparent rate constant k_{app} of the basic hydrolysis of compounds **1** (*1*) and **3** (*2*) *vs.* the concentration of DABCO ($C_{NaOH} = 1 \cdot 10^{-3}$ mol L^{-1}, 25 °C).

Table 1. Constants A and B in equation (1)

Substrate	A	B	r^a
1	0.00211	0.0273	0.956
2[b]	0.00100	0.0180	—
3	0.00156	0.0248	0.983

[a] The correlation coefficient.
[b] The data from Ref. 34.

aquated metal ion to hydroxo complexes (Scheme 2) results in a considerably lower pH value of the solution.[39]

Scheme 2

$$[La(H_2O)_n]^{3+} \leftrightarrow [La(H_2O)_{n-k}(OH)_k]^{(3-k)} + kH^+$$

Even a small amount of lanthanum nitrate ($2 \cdot 10^{-4}$ mol L^{-1}) present in 0.001 *M* NaOH decreases pH from 11.0 to 10.04. Accordingly, the rate constant k_{app} of the basic hydrolysis of phosphonate **2** is four times that of the hydrolysis in the absence of the catalyst at the same pH value. When the concentration of $La(NO_3)_3$ is $2 \cdot 10^{-2}$ mol L^{-1}, the pH value of the alkaline solution decreases to 7.46, and the corresponding k_{app} value shows a 220-fold increase for the basic hydrolysis of compound **1**.

The catalytic effect of the mixed system DABCO (**4**, **5**)—$La(NO_3)_3 \cdot 6H_2O$—0.001 *M* NaOH depends on the degree of hydrophobicity, charge state, and content of the components in solution. With DABCO used in both low and high concentrations, an increase in the content of lanthanum nitrate substantially lowers the pH of the solution (Fig. 2). However, the associated decrease in k_{app} is observed only in the initial segment of the k_{app} *vs.* $C_{La(NO3)3}$ plot (Fig. 3). As the La^{3+} content increases and, consequently, its catalytic impact becomes stronger, this trend is reversed (so k_{app} goes up). In this case, the catalytic effect of the whole system grows especially high (a more than 100-fold increase in the rate constant) (see Fig. 3).

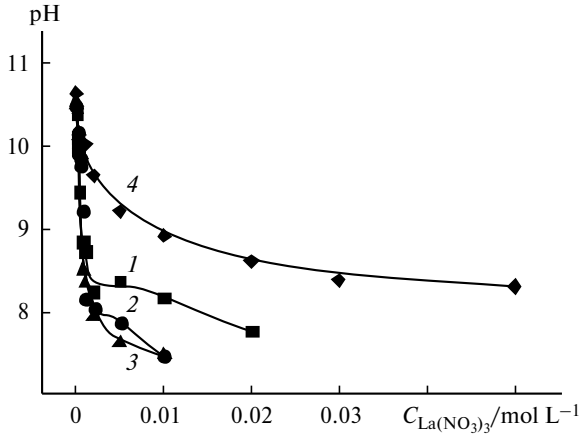


Fig. 2. Plots of the pH of the solutions containing DABCO (**4**, **5**), $La(NO_3)_3 \cdot 6H_2O$, and NaOH *vs.* the concentration of $La(NO_3)_3$ at $C_{DABCO} = 3 \cdot 10^{-3}$ (*1*) and $5 \cdot 10^{-2}$ mol L^{-1} (*4*) and $C_{4,5} = 3 \cdot 10^{-3}$ mol L^{-1} (*2*, *3*) ($C_{NaOH} = 1 \cdot 10^{-3}$ mol L^{-1}, 25 °C).

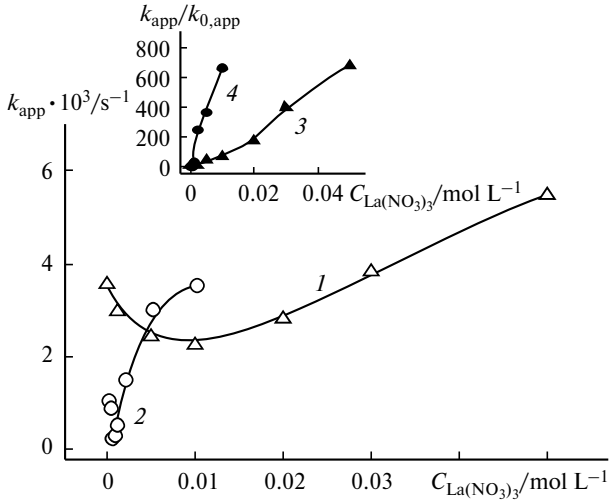


Fig. 3. Plots of the apparent rate constant of the basic hydrolysis of compounds **1** (*1*) and **2** (*2*) in the system DABCO—$La(NO_3)_3 \cdot 6H_2O$—NaOH *vs.* the concentration of $La(NO_3)_3$; the inset: the catalytic effect of the system on the basic hydrolysis of compounds **1** (*3*) and **2** (*4*); $C_{DABCO} = 3 \cdot 10^{-3}$ (*1*, *3*) and $5 \cdot 10^{-2}$ mol L^{-1} (*2*, *4*) ($C_{NaOH} = 1 \cdot 10^{-3}$ mol L^{-1}, 25 °C).

In micellar solutions of mono- and dicationic compounds **4** and **5**, pH abruptly drops with an increase in the La^{3+} content (see Fig. 2). However, the rate constant k_{app} of the basic hydrolysis of phosphonate **2** remains very low, regardless of the increasing concentration of $La(NO_3)_3$, and the whole system shows a catalytic effect only in the presence of surfactant **4** and only at low concentrations of La^{3+} (Fig. 4).

This phenomenon can be due to the structural features of DABCO and its derivatives (**4**, **5**) that include the presence of tertiary N atoms and the charge state of their molecules. When moving from DABCO through MAD **4** to DAD **5**, one can see a decreasing number of the tertiary N atoms and an increasing charge of the molecule, which makes the last two compounds less capable of binding the La^{3+} cations. Moreover, the presence of two tertiary N atoms in DABCO can have some buffering effect on the medium, so pH will decrease less appreciably with an increase in the concentration of $La(NO_3)_3$ (see Fig. 2).

The catalytic effect of the mixed system on the hydrolysis of phosphonates also varies with the content of DABCO and its derivatives. Plots of the apparent rate constants of the basic hydrolysis versus the concentrations of DABCO and its derivatives are shown in Figs 5 and 6. At a low concentration of lanthanum nitrate in solution ($C_{La(NO_3)_3} = 2 \cdot 10^{-4}$ mol L^{-1}), k_{app} initially nearly halved with an increase in the DABCO content; *i.e.*, the catalytic effect weakens (Fig. 7). This can be attributed to a grow-

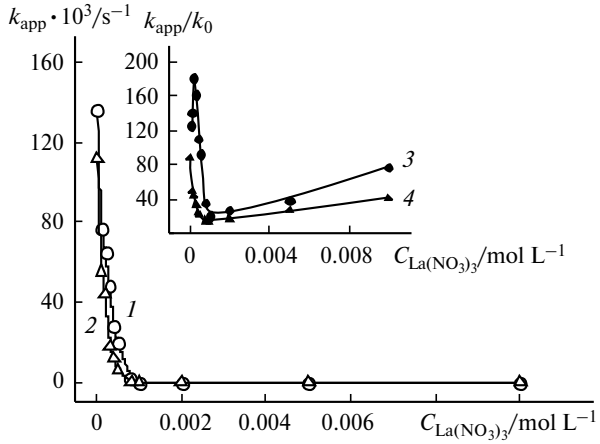


Fig. 4. Plots of the apparent rate constant of the basic hydrolysis of compound **2** in the system surfactant—$La(NO_3)_3 \cdot 6H_2O$—NaOH *vs.* the concentration of $La(NO_3)_3$ (*1*, *2*); the inset: the catalytic effect of the system on the basic hydrolysis of compound **2** (*3*, *4*); the surfactant is **4** (*1*, *3*) and **5** (*2*, *4*) (C_{Surf} = $= 3 \cdot 10^{-3}$ mol L^{-1}, $C_{NaOH} = 1 \cdot 10^{-3}$ mol L^{-1}, 25 °C).

ing fraction of DABCO bound to La^{3+} cations and to a weaker impact of the resulting complex on the hydrolysis. This assumption is substantiated by a twofold increase in k_{app} observed when the DABCO content is four to five times the salt content: the solution contains free DABCO (not bound to the metal), which catalyzes the hydrolysis according to the basic mechanism. At this point, the catalytic effect of the system is the same as that observed in the absence of DABCO. At higher concentrations of DABCO, this effect slightly weakens. The latter can be due to a slight increase in the pH of the solution and, consequently, to an increase in the concentration of hydroxide ions and in $k_{0,app}$ (k_{app} for non-catalytic hydrolysis), which is used as a reference level to calculate the acceleration of the reaction (Fig. 8, *a*).

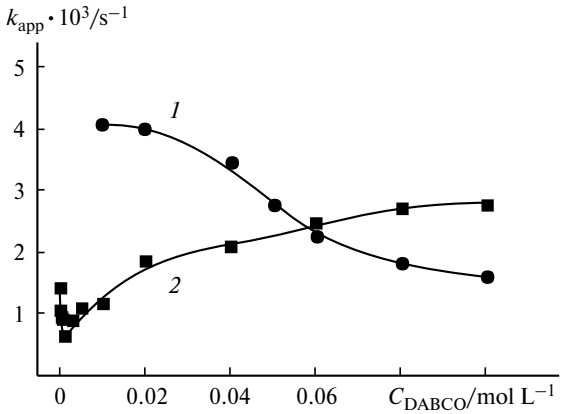


Fig. 5. Plots of the apparent rate constant of the basic hydrolysis of compounds **1** (*1*) and **2** (*2*) in the system DABCO—$La(NO_3)_3 \cdot 6H_2O$—NaOH *vs.* the concentration of DABCO at $C_{La(NO_3)_3} = 2 \cdot 10^{-4}$ (*2*) and $2 \cdot 10^{-2}$ mol L^{-1} (*1*) (C_{NaOH} = $= 1 \cdot 10^{-3}$ mol L^{-1}, 25 °C).

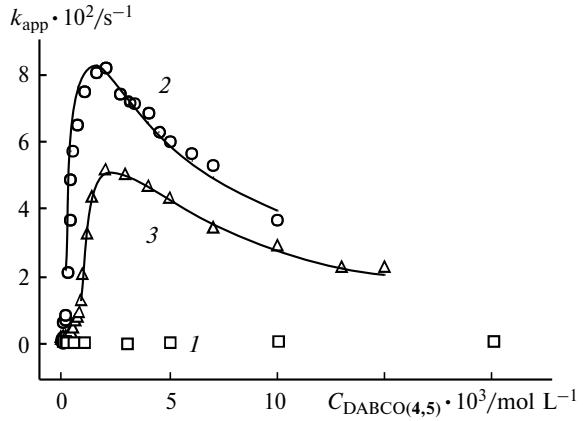


Fig. 6. Plots of the apparent rate constant of the basic hydrolysis of compound **2** in the system DABCO (**4**, **5**)—$La(NO_3)_3 \cdot 6H_2O$—NaOH *vs.* the concentration of DABCO (*1*), **4** (*2*), and **5** (*3*) ($C_{La(NO_3)_3} = 2 \cdot 10^{-4}$ mol L^{-1}, $C_{NaOH} = 1 \cdot 10^{-3}$ mol L^{-1}, 25 °C; the points refer to the experimental data and the curves, to the k_{app} values calculated by Eq. (2)).

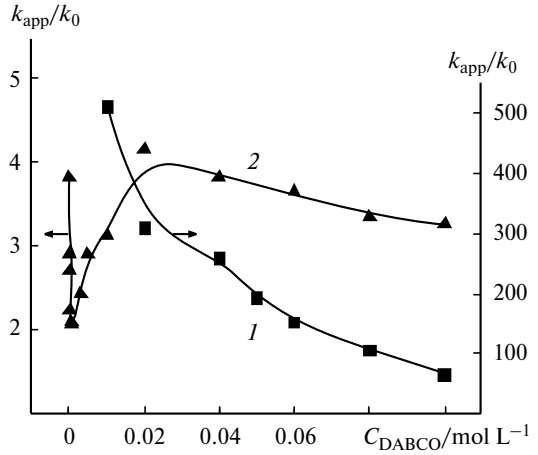


Fig. 7. Plots of the catalytic effect of the system DABCO—$La(NO_3)_3 \cdot 6H_2O$—NaOH on the basic hydrolysis of compounds **1** (*1*) and **2** (*2*) *vs.* the concentration of DABCO at $C_{La(NO_3)_3}$ = $= 2 \cdot 10^{-4}$ (*2*) and $2 \cdot 10^{-2}$ mol L^{-1} (*1*) ($C_{NaOH} = 1 \cdot 10^{-3}$ mol L^{-1}, 25 °C).

A monotonic decrease in k_{app} and in the catalytic effect over a concentration range corresponding to the formation of a La^{3+} complex with DABCO is observed at a high content of lanthanum nitrate as well ($C_{La(NO_3)_3}$ = $= 2 \cdot 10^{-2}$ mol L^{-1}) (see Fig. 7). The diminution of the catalytic effect can also be favored by an appreciable increase in the pH of the solution (see Fig. 8, *a*).

In micellar solutions of surfactants **4** and **5** in the presence of $La(NO_3)_3$, the basic hydrolysis of phosphonate **2** is also catalyzed *via* the micellar mechanism, apart from the basic (or alkaline) and electrophilic ones (see Fig. 6). This is evident from the k_{app} *vs.* $C_{\mathbf{4},\mathbf{5}}$ plots showing two distinctive features. First, k_{app} jumps abruptly at the criti-

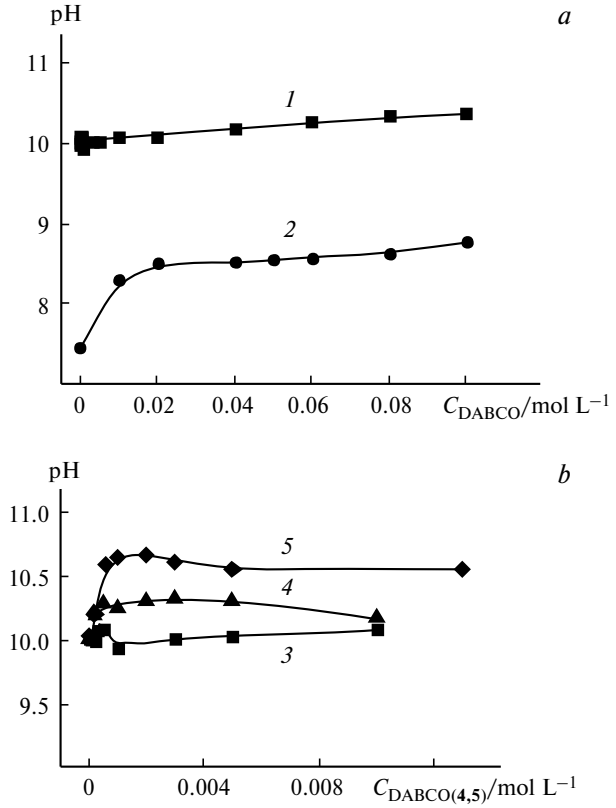


Fig. 8. Plots of the pH of the solutions containing DABCO (**4**, **5**), $La(NO_3)_3 \cdot 6H_2O$, and NaOH *vs.* the concentration of DABCO at $C_{La(NO_3)_3} = 2 \cdot 10^{-4}$ (*1*, *3*) and $2 \cdot 10^{-2}$ mol L^{-1} (*2*) and *vs.* the concentration of compounds **4** (*4*) and **5** (*5*) ($C_{La(NO_3)_3}$ = $= 2 \cdot 10^{-4}$ mol L^{-1}, $C_{NaOH} = 1 \cdot 10^{-3}$ mol L^{-1}, 25 °C); (*a*) the high concentrations of DABCO and (*b*) the low concentrations of DABCO, **4**, and **5**.

cal micelle concentrations (CMC) of surfactants **4** and **5**. Second, both curves have maxima explained by nearly complete binding of these reagents to the aggregates followed by dilution in the micellar pseudophase. We can try to calculate the maximum catalytic effect at a fixed pH value of the mixed system and the corresponding concentration of hydroxide ions. We found that k_{app} and the maximum catalytic effect in the range studied of surfactant concentrations (C_{Surf} = (1—1.5)$\cdot 10^{-2}$ mol L^{-1}) are much higher than those for the solutions of DABCO. For instance, the hydrolysis rate in the presence of the DABCO-containing system increases by a factor of four, while that for the systems containing surfactants **4** and **5** shows a 115- and 36-fold increase, respectively (Table 2).

The experimental data obtained for compounds **4** and **5** (see Fig. 6) were analyzed in terms of the pseudophase model of micellar catalysis (Eqs 2, 3):[40]

$$k_{2,app} = \frac{k_{2,0} + (k_{2,m}/V)K_{Ph}K_{Nu}(C_{Surf} - CMC)}{[1 + K_{Ph}(C_{Surf} - CMC)][1 + K_{Nu}(C_{Surf} - CMC)]}, \quad (2)$$

where $k_{2,app}$ (L mol^{-1} s^{-1}) is the apparent second-order rate constant calculated by dividing k_{app} by the nucleophile concentration; $k_{2,0}$ and $k_{2,m}$ (mol L^{-1} s^{-1}) are the second-order rate constants in the bulk of the solvent and the micellar pseudophase, respectively; V (L mol^{-1}) is the molar volume of the surfactant; K_{Ph} and K_{Nu} (L mol^{-1}) are the constants of binding of the phosphonate and the nucleophile to micelles, respectively; C_{Surf} is the concentration of the surfactant.

The theoretical curves coincide with the experimental data (see Fig. 6). The maximum catalytic effect is described by Eq. (3), which is a modified version of Eq. (2).

$$(k_{app}/k_{0,app})_{max} = \frac{k_{2,m}}{k_{2,0}} \cdot \frac{K_{Ph}K_{Nu}}{V(K_{Ph}^{0.5} + K_{Nu}^{0.5})^2}. \quad (3)$$

The calculated parameters of the micelle-catalyzed basic hydrolysis of compound **2** are given in Table 3. It can be seen that the presence of La^{3+} cations in the system provides a 50% decrease in the apparent rate constant of the hydrolysis in solution ($k_{0,app}$/s^{-1}), a two- to threefold increase in the hydrolysis rate constant in the micellar phase (k_{2m}), an increase in the constants of binding of the substrate (phosphonate) (K_S) and the nucleophile (OH^- ion) (K_{Nu}) to aggregates, and an increase in the CMC. However, the maximum catalytic effect of the system with respect to $k_{0,app}$ ($(k_{app}k_{0,app}^{-1})_{max}$) is somewhat lower. The reason is that a change in the microenvironment of the

Table 2. Catalytic effects of the systems DABCO (**4**, **5**)—$La(NO_3)_3 \cdot 6H_2O$—NaOH on the basic hydrolysis of compound **2** ($C_{La(NO3)3} = 2 \cdot 10^{-4}$ mol L^{-1}, $C_{NaOH} = 1 \cdot 10^{-3}$ mol L^{-1}, 25 °C)

System	$C_{DABCO\ (4,5)}$ /mol L^{-1}	pH	$k_{0,app} \cdot 10^3$* /s^{-1}	$k_{app,DABCO\ (4,5)-La} \cdot 10^2$/s^{-1}	$k_{app,DABCO\ (4,5)-La} \cdot k_{0,app}^{-1}$
No amine	0	10.04	0.39	0.143	3.6
DABCO	0.020	10.10	0.45	0.19	4.2
4	0.002	10.30	0.71	8.2	115
	0.003	10.33	0.76	7.2	95
5	0.002	10.60	1.4	5.1	36
	0.003	10.61	1.45	5.0	34

* The calculated k_{app} value for $k_{2,app} = 3.56$ L mol^{-1} s^{-1}.

Table 3. Parameters of the basic hydrolysis of compound **2** in the system surfactant—NaOH in the absence (pH 11.0) and in the presence of $La(NO_3)_3 \cdot 6H_2O$ at 25 °C ($C_{NaOH} = 1 \cdot 10^{-3}$ mol L^{-1}, $C_{La(NO_3)_3} = 2 \cdot 10^{-4}$ mol L^{-1}, pH 10.02)

Surfactant	C_{La} /mol L^{-1}	$k_{0,app} \cdot 10^3$ /s^{-1}	k_{2m} /L mol^{-1} s^{-1}	$K_S \cdot 10^{-3}$ /L mol^{-1}	$K_{Nu} \cdot 10^{-2}$ /L mol^{-1}	$(k_{app} \cdot k_{0,app}^{-1})_{max}$	F_m	F_c	CMC $\cdot 10^4$ /mol L^{-1}
4[a]	—	3.6	0.56	2.56	1.48	74 (76)[b]	0.18	321	0.8
4	0.0002	1.6	1.7	2.93	2.40	51 (115)[c]	0.107	484	1.4
5[e]	—	3.6	0.45	1.33	1.13	33	0.133	225	3.9
5	0.0002	1.7	1.0	1.51	2.75	29 (36)[d]	0.0657	451	8.2

[a] The data from Ref. 34.
[b,c,d] The maximum catalytic effects of the system relative to the apparent rate of the basic hydrolysis of compound **2** in the absence of the surfactant and $La(NO_3)_3 \cdot 6H_2O$ are given in parentheses (the respective pH values are 10.93, 10.3, and 10.6).
[e] The data from Ref. 35.

reagents passing into the micellar phase (F_m) is detrimental to the reaction. The diminishing contribution of this factor cannot be compensated by the increasing concentration of the reagents (F_c), which contributes to the acceleration of the hydrolysis (see Table 3). Note that $F_m < 1$, while $F_c >> 1$, both in the absence and in the presence of $C_{La(NO3)3}$. This indicates that the factor F_m negatively affects the hydrolysis rate and that the factor F_c is crucial for the catalytic effect of the whole system. In basic solutions of compounds **4** and **5** in the presence of $La(NO_3)_3 \cdot 6H_2O$ ($2 \cdot 10^{-4}$ mol L^{-1}) as well as in solutions of compound **4** in the absence of this salt, the pH values measured at the surfactant concentrations corresponding to the maximum k_{app} values (pH 10.93, 10.3, and 10.6) somewhat differ from those registered in the absence of the surfactant (pH 11.0, 10.02, and 10.02, respectively). The maximum catalytic effects with allowance for the change in pH and, accordingly, in the concentration of hydroxide ions are given parenthetically in the corresponding column of Table 3. These data suggest that the presence of $La(NO_3)_3$ favors the catalysis of the basic hydrolysis of the phosphonates with the monocationic surfactant but only slightly affects the catalytic effect of the system containing the dicationic surfactant.

To sum up, the mixed systems composed of DABCO (or its alkylated derivative), $La(NO_3)_3 \cdot 6H_2O$ ($2 \cdot 10^{-4}$ mol L^{-1}), and NaOH ($1 \cdot 10^{-3}$ mol L^{-1}) catalyze the basic hydrolysis of *O*-alkyl *O*-4-nitrophenyl chloromethylphosphonates. The mechanism of action and efficiency of the catalytic system depend on the structures and relative contents of its component. In the presence of dicationic DAD, an increase in the concentration of La^{3+} ions does not promote the catalysis of the hydrolysis. For the system containing monocationic MAD, its catalytic effect becomes stronger as the lanthanum concentration increases (but only at low concentrations of $La(NO_3)_3$). In the case of DABCO, the La^{3+} ions contribute to the increased catalytic effect of the system over the whole range studied of salt concentrations. The concentration dependence of the catalytic effect for DABCO and its derivatives varies with the type of species (associates) formed in solution. An increase in the DABCO content, which is accompanied by the formation of a La^{3+} complex with DABCO, is unfavorable for the catalysis. The formation of micellar aggregates in solutions of MAD and DAD increases the catalytic effect of the whole system. The catalytic effect due to the concentration of the reagents in the micellar phase increases in the order DABCO < **5** < **4**, and the corresponding rate constant of the hydrolysis in the presence of compound **4** shows a ~115-fold increase.

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