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Catalytic Properties of Micellar Systems Based on 4-Aza-1-Alkyl-1-Azoniabicyclo[2.2.2]octane Bromides

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Abstract—The catalytic effect of micellar systems based on alkylated 1,4-diazabicyclo[2.2.2]octanes on the alkaline hydrolysis of butyl chloromethyl 4-nitrophenyl phosphonate is reported. The catalytic effect is due to the reactants concentrating in the micellar phase. It increases with an increase in the hydrophobicity of the surfactant. The bicyclic surfactant manifests the higher efficiency than its cyclic and noncyclic analogues. The micellization properties of alkylated 1,4-diazabicyclo[2.2.2]octanes in aqueous solutions have been investigated by the NMR method. An increase in the hydrophobicity of the surfactant decreases the critical micelle concentration and increases the hydrodynamic radius and aggregation numbers of the micelles.

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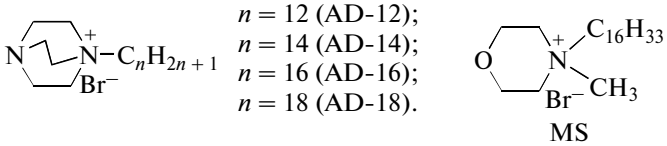
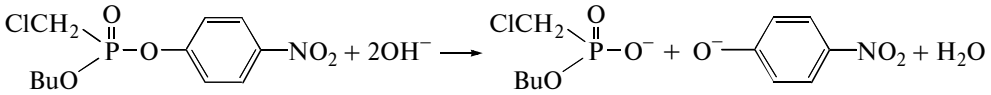
Organized solutions of surfactants find wide use in present-day technologies aimed at producing biomimetic catalytic and sensor systems, protective coatings, nanocontainers, and nonviral vectors [1–3]. The usability of amphiphiles for these purposes is due to their surface activity and their capability for self-organization at the interfaces and in the solution bulk and for solubilization of a wide variety of organic compounds. One of the most promising applications of organized solutions is design of catalytic compositions and synthesis of monodisperse nanoparticles. The efficiency of such systems is largely determined by the choice of the surfactant structure and concentration. Thus, surfactants of the new type and their catalytic activity are of practical interest.

Cationic surfactants substantially affect the rate of ion–molecule reactions through Coulomb interaction with ionic reactants [4]. It is in cationic micelles that efficient catalytic acceleration of nucleophilic substitution reactions, such as the hydrolysis of organic and bioorganic substrates, takes place. At present, the main lines of improvement of micellar catalysts are enhancing the efficiency and selectivity of catalytic systems and reducing the surfactant concentration. This can be achieved by varying the surfactant structure, including the nature of the head group, and by passing to dimeric (geminal) surfactants. Systematic investigation of the influence of the chemical structure of the surfactants on their micellization properties and functional activity is expected to provide insight into the behavior of amphiphilic compounds and to contribute to solution theory.

Hydrophobized derivatives of 1,4-diazabicyclo[2.2.2]octane, which are cationic surfactants with a bicyclic head group, can act as ionic liquids [5] and catalysts for the cleavage of phosphodiester bonds in RNA [6] and for the hydrolysis of 4-nitrophenyl diphenyl phosphate [7]. In the present work, we investigated catalytic systems based on alkylated 1,4-diazabicyclo[2.2.2]octanes (ADs) with different degrees of hydrophobicity. The influence of these surfactants on the alkaline hydrolysis of butyl chloromethyl 4-nitrophenyl phosphonate (BCNP) in aqueous solutions was studied.





A comparative analysis of the influence of the bicyclic structure of the head group of the surfactants on their catalytic effect was performed using cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPB), and a morpholinic surfactant (MS).

The catalytic acceleration of reactions in micellar systems occurs due to the formation of surfactant aggregates and the transfer of the reactants to the micellar pseudophase. Therefore, one of the tasks of our study was to estimate aggregation in solution. For this purpose, we investigated the micellization of the surfactants by pulsed field gradient NMR and analyzed the concentration dependences of the self-diffusion coefficient of the free and micellar components of the surfactants and the distribution of the surfactant molecules over these components.

EXPERIMENTAL

The bicyclic surfactant AD-12 was synthesized by reacting 1,4-diazabicyclo[2.2.2]octane (DABCO) with dodecyl bromide in acetone. An equimolar amount of a dodecyl bromide solution was added dropwise to a stirred solution of DABCO cooled to 18°C. The reaction mixture was stirred for 1 h at room temperature and for 30 min at 45–50°C. Excess solvent was distilled off in vacuo. The resulting salt precipitate was separated by filtration, recrystallized from acetone, and dried in vacuo. The compounds AD-14, AD-16, and AD-18 were synthesized in a similar way and were recrystallized from an acetone–methanol mixture. Their structures were confirmed by elemental analysis, ^{1}H NMR, and IR spectroscopy. The compound MS was obtained by the quaternization of *N*-methylmorpholine with cetyl bromide [8]. BCNP was synthesized via a standard procedure [9]. The surfactants CTAB and CPB (Sigma) were purified by recrystallization from an acetone–ethanol mixture. Bidistilled water was used in the preparation of solutions.

The self-diffusion coefficients of the surfactant molecules in aqueous solutions were measured on an AVANCE 400 NMR spectrometer (Bruker) using a pulsed magnetic field gradient (G) of up to 0.53 T/m. The self-diffusion coefficients (D) were derived from the decrease in the integral intensity of stimulated spin echo signals from protons of various groups of the alkyl and cyclic moieties of AD, which occurred due to the change in the field gradient in a series of three consecutive 90° pulses:

$$I(G) = I_0 \exp\left[-(\gamma\delta G)^2 D\left(\Delta - \frac{\delta}{3}\right)\right],$$

where γ is the gyromagnetic ratio of the nucleus (proton), δ is the gradient pulse duration, and Δ is the time interval between the gradient pulses. Depending on the self-diffusion coefficient values to be measured, δ and Δ were varied from 6 to 10 ms and from 50 to 70 ms, respectively. These times are substantially longer than the time of exchange of molecules between the free and micellar components of the solution. The self-diffusion coefficient of a molecule was determined by averaging the values obtained by an analysis of the proton resonance signals from different moieties. The self-diffusion coefficient measurement error at high surfactant concentrations was ~2%, whereas at low concentrations the error was ~5%. The sample temperature was maintained at 25°C using the temperature control system of the spectrometer.

When analyzing the concentration dependence of the self-diffusion coefficients of the surfactant molecules, we used the pseudophase model of micellization [10], in which the critical micelle concentration (CMC) is considered as the point of transition between the monomeric (free) and aggregated states of the surfactant in solution. Under the conditions of fast exchange between the free and micellar components, the observed self-diffusion coefficient of the surfactant molecules in solution (D_{obs}) can be presented as [11]

$$D_{obs} = p_{fr}D_{fr} + p_mD_m,$$

where p_{fr} and p_m are the fractions of the free and micellar components of the surfactant in the solution and D_{fr} and D_m are the self-diffusion coefficients of the free and micellar components of the surfactant.

The self-diffusion coefficients of micelles is determined using a very small amount of a hydrophobic substance (solubilizate), whose molecules penetrate into the micelles and diffuse together with them [11]. Accordingly, the self-diffusion coefficient of micelles (D_m) is measured as the decrease in the intensity of the NMR line corresponding to protons of the solubilizate. In our experiments, hexamethyldisiloxane $(CH_3)_3SiOSi(CH_3)_3$ (HMDSO) was used as the solubilizate. It is assumed that the presence of solubilizate molecules in the micelles does not cause serious errors in the determination of the self-diffusion coefficients and sizes of the micelles.

The hydrodynamic radius of micelles (R_h) was determined using the Stokes–Einstein equation $R_h = kT/6\pi\eta D_m^0$, where η is the viscosity of deuterated water (1.1 cP at 25°C), and D_m^0 is the self-diffusion coefficient of the micelles determined by the extrapolation of the concentration dependence of D_m to the zero micelle concentration.

The reaction kinetics was studied by UV spectrophotometry as the increase in the absorbance due to the 4-nitrophenolate anion at 400 nm on a Specord UV-Vis spectrophotometer in temperature-controlled cells. The apparent rate constants of the reaction (k_{app}) were determined using a first-order equation. The concentration of the substrate (BCNP) at the beginning of the reaction was 1×10^{-4} mol/l.

The ^{31}P NMR spectra of BCNP and its hydrolysis product were recorded on a Bruker MSL-400 spectrometer (162 MHz). The chemical shifts of the ^{31}P lines of the substrate and products were determined relative to an external standard (H_3PO_4). The phos-

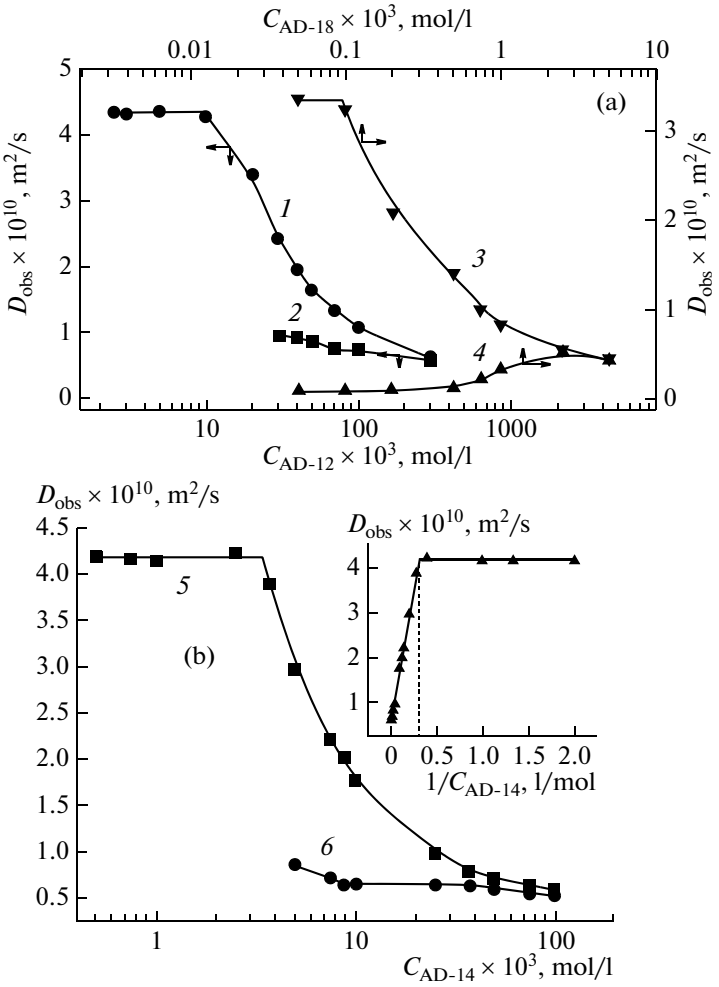


Fig. 1. Observed self-diffusion coefficient of (*1*) AD-12, (*3*) AD-18, (*5*) AD-14, and (*2*, *4*, *6*) HMDSO versus the concentration of (a) AD-12 and AD-18 and (b) AD-14. Inset in Fig. 1b: D_{obs} versus the inverse concentration of AD-14. The measurements were carried out in D_2O solutions at 25°C.

phonate, AD-14, and NaOH concentrations in solutions were 0.02, 0.05, and 0.04 mol/l, respectively. The chemical shift of the ^{31}P line of BCNP is 17.7 ppm.

RESULTS AND DISCUSSION

Self-Organization of the AD-Based Systems

Self-organization in AD solutions was studied as the dependence of the surfactant self-diffusion coefficient on the concentration of amphiphilic molecules. Figure 1 plots the concentration dependences of the self-diffusion coefficient of AD-12, AD-14, and AD-18 molecules dissolved in heavy water and shows the variation of the self-diffusion coefficient of the hydrophobic probe HMDSO, which was used to determine the self-diffusion coefficient of the micelles. The self-diffusion coefficients of all of the compounds remain unchanged up to a certain surfactant concentration identified as CMC. These self-diffusion coefficients are 4.4×10^{-10}, 4.2×10^{-10}, and 3.3×10^{-10} m^2/s for AD-12, AD-14, and AD-18, respectively. This can be considered to be evidence of the monomeric state of the surfactant molecules. The self-diffusion coefficients decrease at concentrations higher than the CMC (Fig. 1), which indicates the self-association of the surfactant molecules. The change in D_{obs} is caused by the decrease in the concentration of free molecules (C_{fr}) and by the increase in the concentrations of molecules in the micelles (C_m). This is confirmed by the concentration dependences of p_{fr} and p_m for AD-12 (Fig. 2). Below the CMC, $C_{fr} = C_{Surf}$; i.e., all surfactant molecules dissolved in water are in the monomeric state ($p_{fr} = 100\%$, $p_m = 0\%$). At the surfactant concentrations higher than the CMC, the compensation character of the dependences is observed: p_{fr} decreases and p_m increases to ~100%.

At high surfactant concentration, the concentration dependences of the surfactant and HMDSO self-diffusion coefficients coincide (Fig. 1), confirming that aggregation takes place. Because the hydrophobic

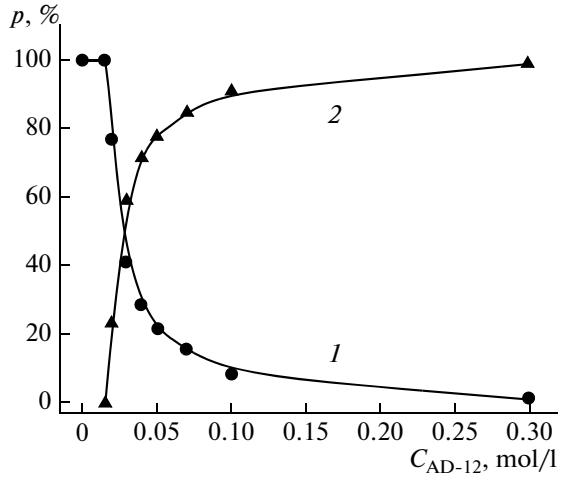


Fig. 2. Fraction of (*1*) free and (*2*) micellized AD-12 molecules versus the surfactant concentration at 25°C.

probe is water-insoluble, the signal from HMDSO is detected only after the CMC of the surfactant is reached, when the probe is solubilized by the micelles, as is observed in the AD-12 and AD-14 solutions. In the solutions of AD-18 at the surfactant concentrations below the CMC, the self-diffusion coefficient of HMDSO is two orders of magnitude lower than the self-diffusion coefficient of the monomeric form of AD-18. Probably, the signal of HMDSO included in the emulsion droplets formed by the probe molecules in the aqueous medium is detected in this concentration range. The smooth increase in the self-diffusion coefficient of the probe with an increase in the surfactant concentration is due to the gradual HMDSO solubilization by the micelles taking place as the concentration of the latter increases.

The CMC value can most precisely be determined from the dependence of D_{obs} on $1/C_{Surf}$ [11]. The thus-determined CMC values for AD-12, AD-14, and AD-18 are 1.5×10^{-2}, 3.4×10^{-3}, and 1.1×10^{-4} mol/l, respectively (see, e.g., inset in Fig. 1b). The CMC of AD-16 measured by us earlier was 8.5×10^{-4} mol/l. The dependence of the CMC on the number of carbon atoms in the surfactant radical (n) is expressed by the formula

$$\log \mathrm{CMC} = A - Bn, \qquad (1)$$

where A and B are constant characteristics of different homological series and different temperatures [12]. The above values of CMC are well described by Eq. (1) (correlation factor of 0.996) at $A = 2.4$ and $B = 0.35$.

The values of R_h for the AD-12 and AD-14 micelles found using the Stokes–Einstein equation are 19.1 and 24.0 Å, respectively. The radii of the AD-12 and AD-14 micelles should be 15.1 and 20.0 Å, respectively with allowance made for the presence of a water monolayer in the hydration shells of the head groups (the diameter of the D_2O molecule was accepted to be 4 Å). We divided the volume of a micelle, $V_m = 4\pi R^3/3$, by the volume of a surfactant molecule, $V_{mol} = M/\rho N_A$, where M is the molecular weight, ρ is the density of the surfactant in the micelles (considered to be equal to the density of the surfactant in the solid state, i.e., 1×10^3 kg/m^3), and N_A is Avogadro's number, and found that the aggregation number N for the AD-12 and AD-14 micelles is 24 and 52, respectively. The parameters R_h and N were not estimated from the measured self-diffusion coefficients of the AD-18 micelles because of the low accuracy of the extrapolation of the concentration dependence of D_m to the zero micelle concentration. The parameters of the emulsion droplets of HMDSO ($M = 162$, $\rho = 764$ kg/m^3) were determined by the same method. In the systems based on AD-18, they were $R_h = 233$ Å and $N = 1.5 \times 10^5$. These data indicate that the HMDSO droplets are considerably larger than the micelles and consist of a great number of molecules. That is why their self-diffusion coefficient is lower than that of the micelles.

Catalytic Effect of the Micellar Systems

The mechanism of the alkaline hydrolysis of butyl chloromethyl 4-nitrophenyl phosphonate is confirmed by the data of UV spectrophotometry and ^{31}P NMR spectroscopy. The formation of the 4-nitrophenolate anion was detected as the appearance of an absorption band at 400 nm during the reaction. The resulting butylchloromethylphosphonic acid is characterized by a ^{31}P NMR signal at $\delta = 13.8$ ppm in the absence of the surfactant and at 13.4 ppm in the presence of AD-14.

The concentration dependences of the apparent rate constant of alkaline hydrolysis in solutions of 0.001 mol/l NaOH in the presence of AD pass through an extremum (Fig. 3a) and are described by the equation of the pseudophase model of micellar catalysis [10]:

$$k_{2,app} = \frac{k_{2,0} + \left(k_{2,m}/V\right) K_S K_{Nu} \left(C_{Surf} - \mathrm{CMC}\right)}{\left(1 + K_S C_{Surf}\right)\left[1 + K_{Nu}\left(C_{Surf} - \mathrm{CMC}\right)\right]}, \qquad (2)$$

where $k_{2,app}$ is the apparent second-order rate constant obtained by dividing k_{app} by the nucleophile concentration; $k_{2,0}$ and $k_{2,m}$ are the second-order rate constants in the solvent bulk and in the micellar pseudophase, respectively; V is the molar volume of the surfactant; and K_S and K_{Nu} are the substrate–micelle and nucleophile–micelle binding constants, respectively.

The parameters calculated using Eq. (2) for the micelle-catalyzed process are given in Table 1. Clearly, $k_{2,m}$ depends weakly on the hydrophobicity of the surfactant. Only the $k_{2,m}$ for AD-12 is somewhat larger than the $k_{2,m}$ values for the other homologues. This is likely explained by the fact that polarity in the locus of the reactants in the micelle changes to a lesser extent than in water. The cetyl homologue is characterized by

the highest binding constant. The binding constant of the hydroxide ion and the maximum acceleration of the process $(k_{app}/k_0)_{max}$ increase with an increasing length of the hydrocarbon radical of the surfactant. In terms of the Berezin model (Eq. (2)), the maximum acceleration of the process is described by the equation

$$\left(k_{app}/k_0\right)_{max} = \frac{k_{2,m}}{k_{2,0}} \frac{K_S K_{Nu}}{V\left(K_S^{0.5} + K_{Nu}^{0.5}\right)^2}, \qquad (3)$$

where the first factor on the right-hand side accounts for the change in the microenvironment of the reactants upon their transfer from the solvent to the micellar phase (factor F_m) and the second factor accounts for the effect of the reactant concentrating in the micellar phase (factor F_c).

According to the data in Table 1, for all surfactants F_m is below unity and F_c ranges from several tens to several hundreds. Rather high values of F_c counterbalance the negative effect of the micellar microenvironment factor. Due to this, the net effect of the micelles, equal to the product of F_c and F_m, is positive and reaches a factor of ~60 with an increasing length of the hydrocarbon radical of AD. The weak effect of the starting nonalkylated 1,4-diazabicyclo[2.2.2]octane on BCNP hydrolysis also indicates the favorable influence of the hydrophobicity of the surfactant with the bicyclic head group. Aqueous solutions of nonalkylated 1,4-diazabicyclo[2.2.2]octane have pH 10.47. The dependence of the apparent first-order reaction rate constant of alkaline hydrolysis of the substrate on the DABCO content (C_D) is linear (Fig. 3a) and is described by the equation $k_{app} = 0.001 + 0.018C_D$. In the DABCO concentration range (<0.1 mol/l), the maximum catalytic effect is 2.8.

In addition to elucidating the influence of hydrophobicity on the catalytic effect of the surfactant, we compared the effects of AD-16 and surfactants having a cyclic or noncyclic head group.

The apparent rate constants of alkaline BCNP hydrolysis in micellar solutions of CPB, MS, and CTAB are shown in Fig. 3b. The rate constant curves tend to a plateau. They were fitted the following equation [13]:

$$k_{app} = \frac{k_m K_S \left(C_{Surf} - CMC\right) + k_0}{1 + K_S(C_{Surf} - CMC)}, \qquad (4)$$

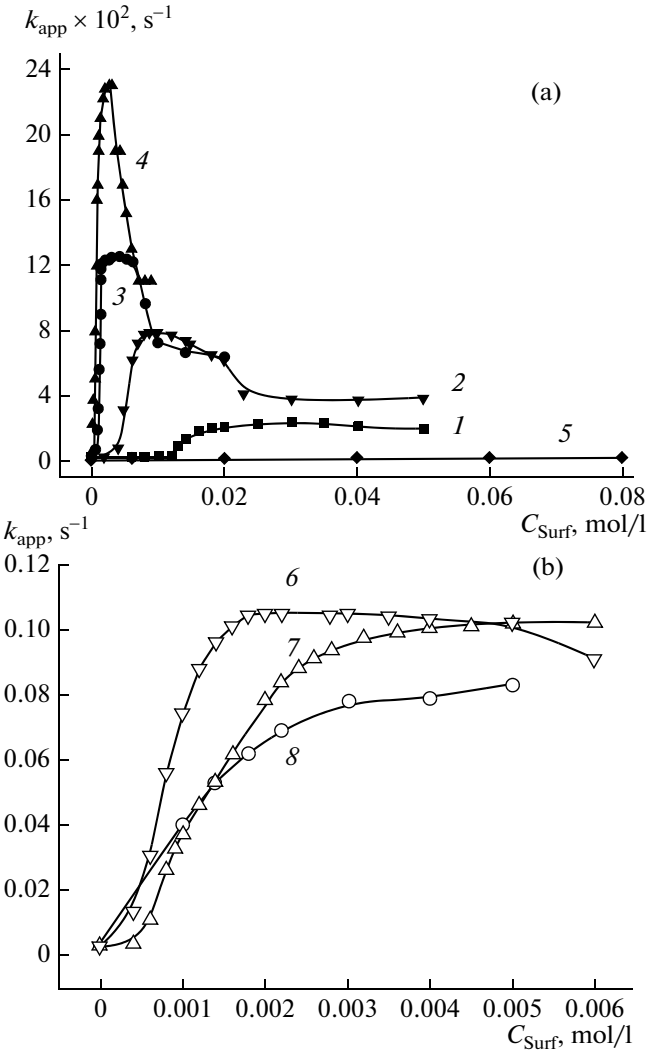


Fig. 3. Apparent rate constant of alkaline BCNP hydrolysis in aqueous alkali solutions of (a) (*1*) AD-12, (*2*) AD-14, (*3*) AD-16, (*4*) AD-18, and (*5*) DABCO and (b) (*6*) CPB, (*7*) MS, and (*8*) CTAB versus the surfactant concentration; $C_{NaOH} = 10^{-3}$ mol/l, 25°C.

where k_m and k_0 are the first-order reaction rate constants in the micellar phase and in the solvent bulk, respectively. The parameters calculated using Eq. (4) are listed in Table 2. Clearly the CMC values for CPB, MS, and CTAB are smaller than those for their bicy-

Table 1. Parameters of the alkaline hydrolysis of BCNP catalyzed by ADs in aqueous solutions of NaOH (0.001 mol/l) at 25°C

Surfactant	$k_{2,m}$, l mol^{-1} s^{-1}	K_S, l/mol	K_{Nu}, l/mol	$(k_{app}/k_0)_{max}$	F_m	F_c	$F_m \times F_c$	CMC × 10^4, mol/l
AD-12	0.91	330	10	7.7	0.29	24.7	7.2	120
AD-14	0.43	2000	96	25	0.14	215	30	46
AD-16	0.48	4570	110	41	0.16	274	42	7.5
AD-18	0.56	2560	148	74	0.18	321	58	0.8

Table 2. Parameters of the alkaline hydrolysis of BCNP catalyzed by the cationic surfactants in aqueous solutions of NaOH (0.001 mol/l) at 25°C

Surfactant	k_m, s^{-1}	K_S, l/mol	CMC × 10^4, mol/l	k_m/k_0
CPB	0.13	2400	4.9	37
MS	0.10	1300	5.7	29
CTAB	0.099	1200	4.6	28

clic analogue (AD-16, see Table 1); i.e., the micellization of the latter is somewhat more difficult. However, the constant of binding of the substrate with the micelles of the bicyclic surfactant and the catalytic effect of the latter on the alkaline hydrolysis of BCNP are higher than those of the cyclic surfactants and CTAB (compare Tables 1 and 2).

It was of interest to carry out BCNP hydrolysis catalyzed by AD micelles at a lower alkalinity of the solution, i.e., under milder conditions. For this purpose, we studied the decomposition of the phosphorus substrate in the borate buffer at pH 9.18 in the presence of AD-18. In this case, the situation is complicated by the possibility that BCNP hydrolysis is accompanied by the interaction of the substrate with the buffer component of the solution (tetraborate anion). In this case, the contribution from this interaction depends on the concentrations of both the borax and surfactant (Figs. 4, 5). A decrease in the borax concentration decreases k_{app} of the catalyzed reaction (Fig. 4), and the extrapolation of these dependences to the zero borax content makes it possible to determine k_{app} for the hydrolysis of the substrate. The plots of the apparent rate constant of BCNP decomposition versus $C_{AD\text{-}18}$ at different borax concentrations are shown in Fig. 5. As in the case of the above-described alkaline solutions (Fig. 3a), k_{app} as a function of the surfactant concentration passes through an extremum and is described by Eq. (2). The parameters calculated using Eqs. (2) and (3) for the catalyzed reaction are presented in Table 3. The decrease in the borax content of the solution is accompanied by an increase in the reaction rate constant in the micellar pseudophase, in the substrate–micelle binding constant, and in the catalytic effect of the aggregates. The strongest catalytic effect, characterized by a factor of 220, is achieved when the buffer component of the solution is entirely absent. This demonstrates that the micellar aggregates of the bicyclic surfactant exert a stronger effect the hydrolysis of BCNP in less alkaline solutions. In addition, as in the 0.001 M NaOH solutions, in the borate buffer solutions the catalytic effect of the micellar aggregates on the hydrolysis process is governed by reactant concentrating in the micellar pseudophase (Tables 1, 3).

Thus, the concentration dependence of the self-diffusion coefficient of the molecules of alkylated 1,4-diazabicyclo[2.2.2]octanes in aqueous solutions was studied by the NMR method. The critical micelle concentrations, hydrodynamic radii, and aggregation numbers of the micelles were determined. With an increasing number of carbon atoms in the alkyl radical chain of the AD molecules, the self-diffusion coefficients of the monomeric molecules (below CMC) and the CMC of the surfactants decrease. The cationic surfactants catalyze the hydrolysis of butyl chlorome-

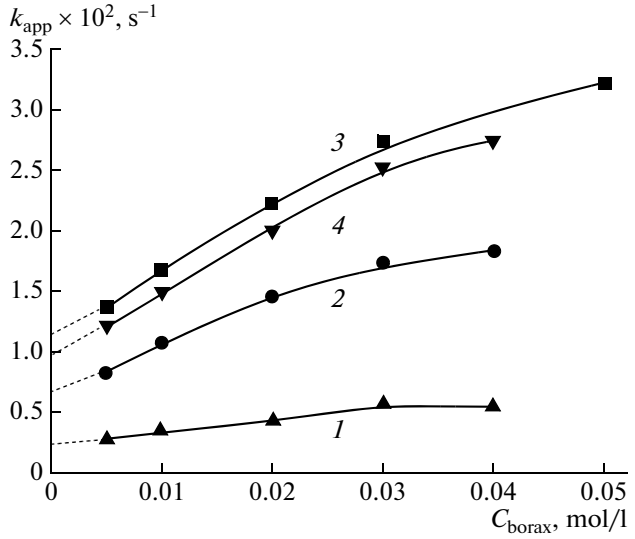


Fig. 4. Apparent rate constant of the nucleophilic substitution in BCNP in micellar solutions of AD-18 versus the borax concentration at AD-18 concentrations of (*1*) 2×10^{-4}, (*2*) 6×10^{-4}, (*3*) 2×10^{-3}, and (*4*) 5×10^{-3} mol/l; borate buffer, pH 9.18, 25°C.

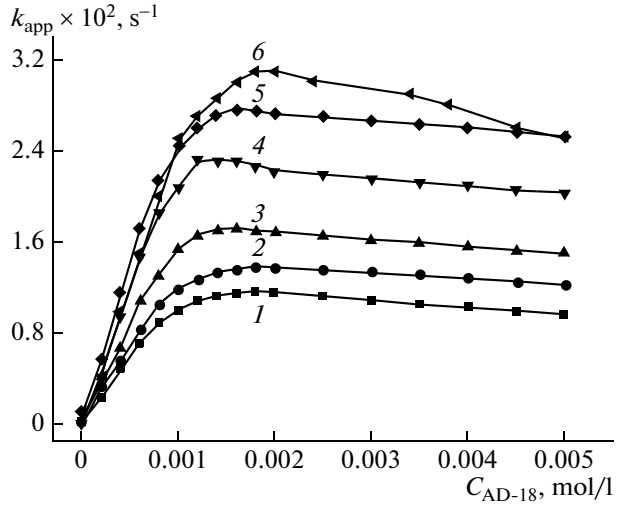


Fig. 5. Apparent rate constant of the nucleophilic substitution in BCNP in micellar solutions of AD-18 versus C_{Surf} at borax concentrations of (*1*) 0, (*2*) 5×10^{-3}, (*3*) 1×10^{-2}, (*4*) 2×10^{-2}, (*5*) 3×10^{-2}, and (*6*) 5×10^{-2} mol/l; pH 9.18, 25°C.

Table 3. Parameters of the nucleophilic substitution in BCNP catalyzed by AD-18 in borate buffer solutions at pH 9.18 and 25°C

C_{borax}, mol/l	$k_{2,m}$, l mol^{-1} s^{-1}	K_S, l/mol	K_{Nu}, l/mol	$(k_{app}/k_0)_{max}$	F_m	F_c	$F_m \times F_c$	CMC × 10^4, mol/l
0	2.1	1550	204	220	0.59	366	220	1.8
0.005	0.0085	1030	201	40	0.13	323	40	1.4
0.01	0.0048	854	252	41	0.11	353	40	1.4
0.02	0.0029	825	310	39	0.1	398	40	1.5
0.03	0.0024	750	323	37	0.094	392	37	1.4
0.05	0.0018	495	319	28	0.084	328	27	1.7

thyl 4-nitrophenyl phosphonate. Their catalytic activity depends on the structure of the head group of the surfactant and increases in the order CTAB ≈ MS < CPB < AD-16. The catalytic effect of aggregates of alkylated 1,4-diazabicyclo[2.2.2]octanes increases with an increase in their hydrophobicity and with a decrease in the alkalinity of the solution and can enhance the reaction rate by a factor of several hundreds.

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