

## Alkylated Polyethyleneimine–Cationic Surfactant–Calix[4]resorcinarene–Chloroform Catalytic System

E. P. Zhil'tsova\*, R. R. Kashapov, L. Ya. Zakharova, S. S. Lukashenko, A. P. Timosheva,  
E. M. Kasymova, A. R. Kayupov, and A. R. Burilov

Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center,  
Russian Academy of Sciences, Kazan, 420088 Tatarstan, Russia

e-mail: Zhiltsova@iopc.ru

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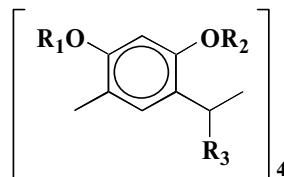
**Abstract**—The kinetics of phosphorylation of alkylated polyethyleneimine in chloroform in the presence of cationic surfactants with a cyclic or bicyclic head group and alkylated calix[4]resorcinarenes has been investigated by UV spectrophotometry. The catalytic activity of individual and mixed solutions of the amphiphilic admixtures depends on the structure of the constituents of the composition, on their concentrations in the solution, and on their relative amounts. In the presence of a calixarene, a decrease in the surfactant and polymer concentrations enhances the catalytic effect of the system.

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The polymer–colloid complexes that form in solutions of polymers and nonmacromolecular amphiphilic compounds as a result of noncovalent interactions can function as nanoreactors producing metal nanoparticles [1] and catalysts for the hydrolysis of phosphorus acid esters [2, 3] and 2-(4-alkoxyphenyl)-1,3-dioxolanes [4]. The amphiphilic component can be a conventional surfactant (anionic, cationic, or nonionic) [5], a pyrimidinophane [6, 7], or a calixarene [8, 9]. In the latter case, in addition to the sorption and solubilization binding of the reactants by the polymer–colloid

aggregates, there can be inclusion-type interactions [5] that enhance the reactant concentrating effect and are thus favorable for the catalytic action of the system.

Here, we report the catalytic activity of supramolecular systems based on alkylated polyethyleneimine, cationic surfactants with different structures, and calix[4]resorcinarenes (CRs) with 2-hydroxyethoxy and phosphorus-containing substituents on the upper rim and alkyl substituents on the lower rim of the macromolecule in chloroform.



**CR-1:** R<sub>1</sub> = R<sub>2</sub> = C<sub>2</sub>H<sub>4</sub>OH, R<sub>3</sub> = n-C<sub>9</sub>H<sub>19</sub>

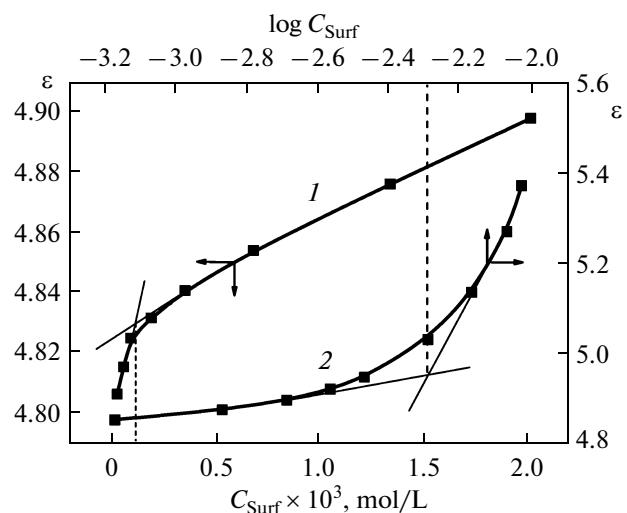
**CR-2:** R<sub>1</sub> = C<sub>2</sub>H<sub>4</sub>OH,

R<sub>2</sub> = C<sub>2</sub>H<sub>4</sub>OP(O)(OH)CH<sub>2</sub>Cl, R<sub>3</sub> = n-C<sub>9</sub>H<sub>19</sub>

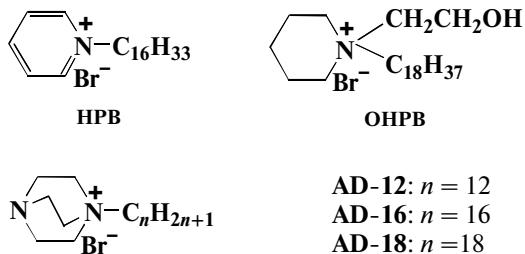
**CR-3:** R<sub>1</sub> = R<sub>2</sub> = C<sub>2</sub>H<sub>4</sub>OH, R<sub>3</sub> = n-C<sub>7</sub>H<sub>15</sub>

The polymer component was branched polyethyleneimine modified with alkyl (*n*-tetradecyl) substituents (APEI). The molar mass of its unit was 229. The degree of substitution (ratio of the number of substituted polyethyleneimine fragments to the number of unsubstituted fragments) was 0.6. The surfactants had a

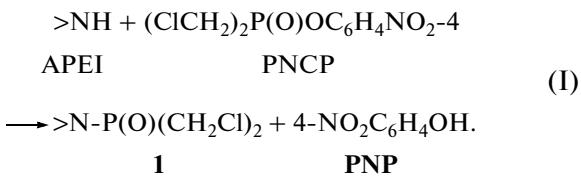
cyclic or bicyclic head. The former group of surfactants consisted of hexadecylpyridinium bromide (HPB) and *N*-octadecyl-*N*-(2-hydroxyethyl)piperidinium bromide (OHPB), and the latter consisted of alkylated derivatives of 1,4-diazabicyclo[2.2.2]octane (AD-12, AD-16, and AD-18):



**Fig. 1.** Relative permittivity of AD-16 solutions in chloroform in the presence of  $8 \times 10^{-5}$  mol/L CR-3 at (1) low and (2) high surfactant concentrations at 25°C.



The catalytic activity of the systems based on APEI, a surfactant, and CR was studied for APEI phosphorylation with 4-nitrophenyl bis(chloromethyl)phosphinate (PNCP):



Interest in this process stems from the fact that phosphorylated polyethyleneimines are usable as complexing agents for uranium ions [10, 11], as components of systems with high proton conductivity [12], and as DNA transporters [13].

In order to elucidate the nature of the catalytic action of the supramolecular compositions by dielectrometry and dielectrometric titration, these compositions were examined in the colloidal state.

## EXPERIMENTAL

APEI was obtained by reacting branched polyethyleneimine (molar mass of 10000) with *n*-tetradecyl bromide [14]. The molar mass of the monomer unit of polyethyleneimine was determined by potentiometric

titration [15, 16]. HPB (Sigma) was purified by recrystallization from an acetone–ethanol mixture. OHPB, AD-12, AD-16, and AD-18 were synthesized by reacting an alkyl bromide with an amine [17, 18]. The synthesis of the calix[4]resorcinarenes CR-1 and CR-2 was described in [19]; the synthesis of PNCP, in [20]. The calixarene CR-2 was obtained by reacting CR-1 with the phosphonic acid dichloroanhydride  $\text{ClCH}_2\text{P}(\text{O})\text{Cl}_2$  in chloroform in the presence of triethylamine at a reactant ratio of 1 : 4 [21]. Chloroform was purified using a standard procedure [22].

Reaction kinetics was studied on a Specord UV-Vis spectrophotometer. Rate constants were determined using a first-order equation. The PNCP concentration in the kinetic experiments was  $5 \times 10^{-5}$  to  $1.4 \times 10^{-4}$  mol/L. The polyethyleneimine concentration (mol/L) was calculated in terms of the molar mass of a monomer unit.  $^{31}\text{P}$  NMR spectra were recorded on a Bruker MSL-400 spectrometer (162 MHz) using  $\text{H}_3\text{PO}_4$  as the external standard.

Dielectrometric titration was carried out by a standard procedure [23]. The relative permittivity of solutions was determined using a setup that contained an E12-I beating-based device and a measurement cell as a temperature-controlled capacitor [24]. The error of determination of the critical micelle concentration (CMC) for surfactants depended on the accuracy with which the solutions (prepared by the serial dilution method) were adjusted to the preset solute concentrations and on the accuracy of relative permittivity measurements in these solutions. The total error in CMC did not exceed 2%.

## RESULTS AND DISCUSSION

### Aggregation Behavior of the Systems

We established in an earlier study that APEI in chloroform undergoes stepwise association and that the critical association concentrations are  $6 \times 10^{-5}$  mol/L ( $\text{CAC}_1$ ) and  $8 \times 10^{-3}$  mol/L ( $\text{CAC}_2$ ) [25]. The CMC values for CR-1, CR-2, and CR-3 in chloroform are  $4.5 \times 10^{-5}$ ,  $3.4 \times 10^{-5}$ , and  $3.5 \times 10^{-5}$  mol/L, respectively [26, 27]. It was determined by dielectrometry and dielectrometric titration that association also takes place in solutions of the surfactants and in the same solutions containing APEI and a calixarene. The concentration dependences of the relative permittivity of the solutions examined are plotted in Fig. 1. The inflections in the curves may be due to changes in the colloidal state of the system and can be explained in terms of the formation of inverse micelle type aggregates. Table 1 lists the CMC data for individual surfactants derived from the inflection point positions, which indicate micellization ( $\text{CMC}_1$ ) and micelle restructuring ( $\text{CMC}_2$ ), and the CAC values for AD-16 + polymer, AD-16 + calixarene, and AD-16 + polymer +

**Table 1.** CMC and CAC data for the systems based on cationic surfactants, APEI, and calixarene in chloroform at 25°C

Surfactant	CMC <sub>1</sub> × 10 <sup>4</sup> , mol/L	CMC <sub>2</sub> × 10 <sup>3</sup> , mol/L	System*	CAC <sub>1</sub> × 10 <sup>5</sup> , mol/L	CAC <sub>2</sub> × 10 <sup>3</sup> , mol/L
AD-12	1.9	5.9	AD-16–APEI	16	8.1
AD-16	2.0	7.5	AD-16–CR-3	9.0	5.0
AD-18	1.6	7.0	AD-16–APEI–CR-3	9.0	5.0

\*  $C_{\text{APEI}} = 5.0 \times 10^{-3}$  mol/L,  $C_{\text{CR-3}} = 8.0 \times 10^{-5}$  mol/L.

**Table 2.** Chemical shift data for the products of the reaction between APEI and PNCP in chloroform in the presence and absence of a surfactant and CR at 25°C

System	δ, ppm ( <sup>31</sup> P)	System	δ, ppm ( <sup>31</sup> P)
APEI	23.4*	APEI–AD-18	22.4
APEI–HPB	22.7	APEI–CR-1**	23.8
APEI–OHPB	23.2	APEI–CR-2**	23.9, 21.0
APEI–AD-12	22.4	CR-2***	19.9
APEI–AD-16	22.4	PNCP***	39.5

Note: Component concentrations, mol/L: APEI, 0.15; surfactant, 0.1; CR, 0.01; PNCP, 0.03.

\* Data from [18].

\*\*  $C_{\text{APEI}} = 0.1$  mol/L.

\*\*\* Chemical shifts for CR-2 and PNCP in chloroform.

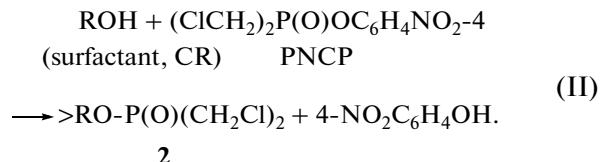
calixarene compositions (CAC<sub>1</sub> and CAC<sub>2</sub>). It is clear from these data that an increase in the length of the hydrocarbon radical in AD and CR exerts only a weak effect on their CMC. The CAC value for the AD-16–polymer system differs only slightly from the CMC of AD-16. The presence of a calixarene (AD-16–CR-3 system) or both the calixarene and polymer (AD-16–APEI–CR-3 system) in the solution favors the aggregation of the surfactant. These data indicate the formation of combined structures in the mixed solutions.

#### Catalytic Properties of the Micellar Systems

The one-component and mixed aggregates forming in the solutions produce an effect on APEI phosphorylation with 4-nitrophenyl bis(chloromethyl)phosphonate (reaction (I)). The reaction yields 4-nitrophenol (PNP) and product **1**. This is indicated by UV spectrophotometric data (appearance of absorption bands at  $\lambda = 310$ –330 and 380–420 nm during the reaction) and by <sup>31</sup>P NMR data. Table 2 lists the chemical shifts for the reaction products in the APEI solution and in the APEI–surfactant and APEI–CR mixed solutions. In all cases, the reaction yields a single product characterized by a chemical shift of  $\delta = 22.4$ –23.9 ppm, which is characteristic of N–H bond phosphorylation products [29]. The presence of a signal at  $\delta = 21.0$  ppm in the spectrum of the reaction products in the APEI–CR-2 system is explained by the presence of the phosphorus-containing substituent in the macrocyclic molecule. The

chemical shift for this macrocycle in chloroform is 19.9 ppm (Table 2).

The following reaction is also possible in the solutions containing OHPB or CR, whose molecules have reactive OH groups:



**2**

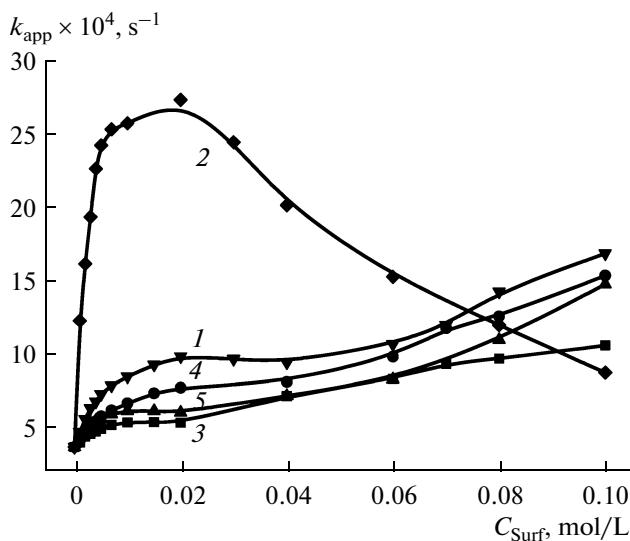
However, if the transesterification product **2** actually formed via the interaction between the phosphonate and the hydroxyalkyl surfactant or CR in chloroform, there would be a characteristic signal at 40 ppm in the NMR spectrum [29]. In fact, this signal was missing (Table 2).

As was demonstrated in an earlier work [30], the dependence of the apparent rate constant of the reaction ( $k_{\text{app},0}$ , s<sup>-1</sup>) on the polyethyleneimine concentration in chloroform is described by the equation

$$k_{\text{app},0} = k_{1,\text{PEI}} C_{\text{PEI}} + k_{2,\text{PEI}} C_{\text{PEI}}^2, \quad (1)$$

where  $k_{1,\text{PEI}} = 0.034$  L mol<sup>-1</sup> s<sup>-1</sup> and  $k_{2,\text{PEI}} = 0.13$  L mol<sup>-2</sup> s<sup>-1</sup> (25°C).

The cationic surfactants speed up the process (Fig. 2). The apparent rate constant of APEI phosphorylation in the solutions of the surfactants as a function of surfactant concentration passes through a maximum (for OHPB) or is still more complicated (for HPB and AD). In the latter case, as the surfactant concentration



**Fig. 2.** Apparent rate constant of the reaction between APEI and PNCP in chloroform in the presence of (1) HPB, (2) OHPB, (3) AD-12, (4) AD-16, and (5) AD-18 as a function of the surfactant concentration ( $C_{\text{APEI}} = 0.01 \text{ mol/L}$ ,  $25^\circ\text{C}$ ).

in the solution is raised,  $k_{\text{app}}$  initially increases and then the curve tends to flatten out in the  $C_{\text{Surf}} = 0.015\text{--}0.05 \text{ mol/L}$  range. This kind of concentration dependence is typical of micelle-catalyzed processes and is explicable in terms of complete substrate binding by the surfactant aggregates [31]. As the surfactant concentration is further increased,  $k_{\text{app}}$  increases again. This may be due to the restructuring of the resulting aggregates [32]. The catalytic activity of the cationic surfactants in the APEI solutions is explained by the formation of polymer–colloid complexes in the systems and by substrate passing from the solvent bulk into aggregates. The joint effect of reactant concentration in the polymer–colloid aggregates and of the change in the microenvironment of the reactants as a result of their passage from the solvent bulk into the aggregates changes the apparent rate constant of the process, making it obey the following equation [31]:

$$\frac{k_{\text{app}} - k_{\text{app},0}}{k_{\text{m}} - k_{\text{app}}} = K_{\text{S}} (C_{\text{Surf}} - \text{CMC}), \quad (2)$$

**Table 3.** Parameters of the reaction between APEI and PNCP in solutions of cationic surfactants in chloroform at  $C_{\text{APEI}} = 0.01 \text{ mol/L}$  and  $25^\circ\text{C}$ , calculated using Eq. (2)

Surfactant	$k_{\text{m}} \times 10^3, \text{s}^{-1}$	$K_{\text{S}}, \text{L/mol}$	$\text{CMC} \times 10^4, \text{mol/L}$	$k_{\text{m}}/k_{\text{app},0}$
HPB	$1.10 \pm 0.02$	$210 \pm 11$	2.2	3.1
AD-12	$0.630 \pm 0.021$	$170 \pm 20$	2.5	1.8
AD-16	$0.930 \pm 0.014$	$110 \pm 22$	2.6	2.7
AD-18	$0.690 \pm 0.012$	$290 \pm 18$	2.1	2.0

where  $k_{\text{m}}$  is the rate constant of the reaction in the colloidal phase,  $K_{\text{S}}$  is the substrate–aggregate binding constant, and  $C_{\text{Surf}}$  is the surfactant concentration.

Table 3 presents the parameters of the catalyzed process calculated via Eq. (2) for surfactant concentrations below those causing the restructuring of the systems. In the case of the OHPB solutions, the apparent rate constant as a function of surfactant concentration passes through a maximum and is described by Eqs. (3) and (4) [33, 34]:

$$k_{2,\text{app}} = \frac{k_{2,0} + (k_{2,\text{m}}/V) K_{\text{S}} K_{\text{Nu}} C}{(1 + K_{\text{S}} C)(1 + K_{\text{Nu}} C)}, \quad (3)$$

where  $k_{2,\text{app}}$  ( $\text{L mol}^{-1} \text{s}^{-1}$ ) is the apparent second-order rate constant obtained by dividing  $k_{\text{app}}$  by the concentration of the nucleophile  $\text{Nu}$ ,  $k_{2,0}$  and  $k_{2,\text{m}}$  are the second-order rate constants for the solvent bulk and polymer–colloid pseudophase,  $V(\text{L/mol})$  is the molar volume of the surfactant,  $K_{\text{S}}$  and  $K_{\text{Nu}}$  ( $\text{L/mol}$ ) are the substrate–aggregate and nucleophile–aggregate binding constants, and  $C$  is the total surfactant concentration minus CMC;

$$(k_{\text{app}}/k_0)_{\text{max}} = \frac{k_{2,\text{m}}}{k_{2,0} V} \frac{K_{\text{S}} K_{\text{Nu}}}{(K_{\text{S}}^{0.5} + K_{\text{Nu}}^{0.5})^2}, \quad (4)$$

where  $(k_{\text{app}}/k_0)_{\text{max}}$  is the maximum acceleration of the process. The first multiplier on the right-hand side of Eq. (4) accounts for the effect of the change in the microenvironment of the reactant upon their passage from the solvent into the colloidal phase (factor  $F_{\text{m}}$ ); the second one, for reactant concentration in the colloidal phase (factor  $F_{\text{c}}$ ).

The process parameters calculated using Eqs. (3) and (4) are listed in Table 4.

The substrate–aggregate binding constant is 100–300  $\text{L/mol}$  (Table 2). The rate constant of the reaction in the colloidal phase and the catalytic effect of the system ( $k_{\text{m}}/k_{\text{app},0}$ ) change in the following order: AD-12  $\approx$  AD-18  $<$  AD-16  $\approx$  HPB. The highest activity in the homologous series of bicyclic surfactants is shown by AD-16. HPB and AD-16, whose head group is cyclic and bicyclic, respectively, display similar cat-

**Table 4.** Parameters of the APEI phosphorylation reaction in OHPB solutions in chloroform at  $C_{\text{APEI}} = 0.01 \text{ mol/L}$  and  $25^\circ\text{C}$ , calculated using Eqs. (3) and (4)

$k_{2,m} \times 10^3$ , $\text{L mol}^{-1} \text{s}^{-1}$	$K_S$ , $\text{L/mol}$	$K_{\text{Nu}}$ , $\text{L/mol}$	$k_{\text{app,max}}/k_{\text{app,0}}$	$\text{CMC} \times 10^4$ , $\text{mol/L}$	$F_m$	$F_c$	$F_m F_c$
$3.8 \pm 0.1$	$670 \pm 65$	$33 \pm 3$	7.8	7.9	0.108	72.9	7.9

**Table 5.** Dependence of the catalytic effect of the APEI–AD-16–CR-2 system on the CR concentration

$C_{\text{CR}}$ , mol/L	$k_{\text{PEI-CR}}/k_{\text{PEI}}$	$k_{\text{PEI-Surf-CR}}/k_{\text{PEI}}$	$k_{\text{PEI-Surf-CR}}/k_{\text{PEI-CR}}$	$k_{\text{PEI-Surf-CR}}/k_{\text{PEI-Surf}}$
0	1.0	2.3	—	1.0
0.0005	1.7	2.9	1.7	1.3
0.002	2.0	4.1	2.0	1.8
0.004	1.8	3.9	2.1	1.7
0.007	0.52	1.6	2.9	0.68
0.01	0.055 (18)*	0.27 (3.7)*	4.7	0.12

Note:  $25^\circ\text{C}$ ,  $C_{\text{APEI}} = 0.01 \text{ mol/L}$ ,  $C_{\text{Surf}} = 0.4 \text{ mol/L}$ .

\* The number in parentheses is the factor by which the reaction rate decreases because of the inhibiting effect of the aggregates.

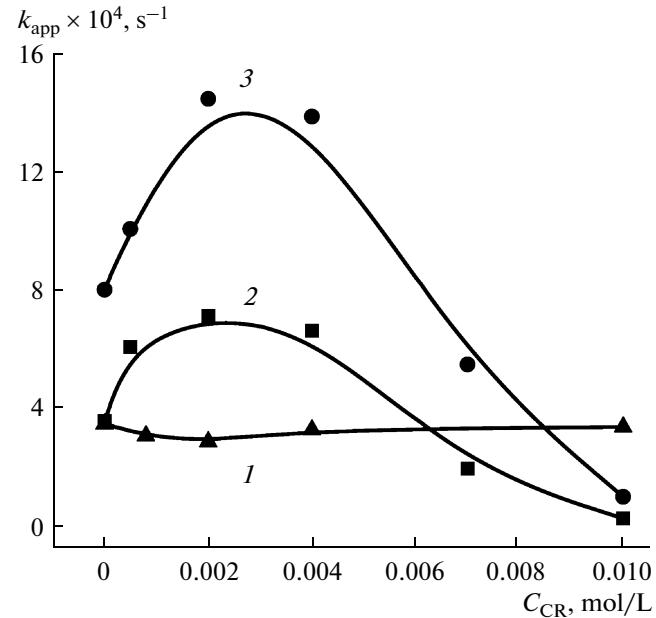
alytic activities. This trend persists at higher surfactant concentrations ( $>0.05 \text{ mol/L}$ , Fig. 2), where the catalytic effect of the system increases (the reaction is accelerated by a factor of 4–5).

A still stronger catalytic effect is observed in APEI phosphorylation in the OHPB solutions (Fig. 2, Table 4). In this case, the substrate–aggregate binding constant is larger than those presented in Table 3 and the reactant concentration factor  $F_c$  in the polymer–colloid phase is as large as 73. However, the microenvironmental factor is  $F_m < 1$ ; that is, it has an adverse effect on the process. The net effect of these factors, which is equal to the product  $F_c F_m$  (Eq. (4)), is 7.9.

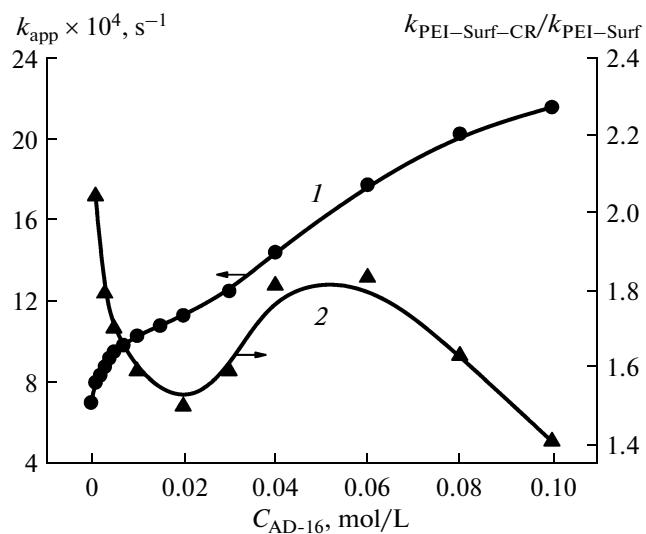
The amphiphilic calixarenes, which, like the surfactants, form association species in chloroform, differ in their effect on APEI phosphorylation. CR-1 practically does not change the  $k_{\text{app}}$  value throughout the concentration range examined (Fig. 3, curve 1). The effect of CR-2 depends on its concentration (Fig. 3, curve 2). As  $C_{\text{CR}}$  is increased,  $k_{\text{app}}$  initially grows, then passes through a maximum at  $C_{\text{CR}} = 0.002\text{--}0.003 \text{ mol/L}$ , and then decreases to become smaller than in the absence of CR. Owing to the catalytic effect of CR-2 ( $C_{\text{CR}} = 0.002 \text{ mol/L}$ ), the rate of the reaction increases by a factor of up to 2 in the absence of a surfactant and by a factor of 4 in the presence of AD-16 (Table 5). At the same time, the inhibiting effect of CR-2 in the macrocycle concentration range examined can diminish the reaction rate by a factor of up to 18 and, in the presence of a surfactant, by a factor of 3.7 (at  $C_{\text{CR}} = 0.01 \text{ mol/L}$ ). These data suggest that, as the macrocycle concentration in the APEI–CR-2–surfactant mixed solutions is increased, the surfactant effect on

the process ( $k_{\text{PEI-Surf-CR}}/k_{\text{PEI-CR}}$  ratio) increases (Table 5) and the effect of CR ( $k_{\text{PEI-Surf-CR}}/k_{\text{PEI-Surf}}$  ratio) initially increases and then decreases down to values indicating an adverse (inhibiting) effect (Fig. 3, curve 3; Table 5).

The macrocycle effect on the process in the APEI–CR-2–surfactant mixed system depends on the sur-



**Fig. 3.** Apparent rate constant of the reaction between APEI and PNCP in chloroform in the presence of (1) CR-1, (2) CR-2, and (3) CR-2 + 0.4 mol/L AD-16 as a function of the calixarene concentration ( $C_{\text{APEI}} = 0.01 \text{ mol/L}$ ,  $25^\circ\text{C}$ ).



**Fig. 4.** (1) Apparent rate constant of the reaction between APEI and PNCP in chloroform in the APEI–CR-2–AD-16 system and (2) the contribution from the calixarene to the catalytic effect of the system as a function of the surfactant concentration ( $C_{\text{APEI}} = 0.01 \text{ mol/L}$ ,  $C_{\text{CR-2}} = 0.002 \text{ mol/L}$ ,  $25^\circ\text{C}$ ).

factant and polymer concentrations as well. The presence of the calixarene in the polymer + surfactant solution enhances the catalytic effect of the system throughout the surfactant concentration range examined (Figs. 2, 4, Table 6). However, the CR effect depends on the AD-16 concentration in the solution. Raising the surfactant concentration initially causes a decrease in the contribution from the macrocycle to the catalytic effect (Fig. 4). At the AD-16 concentrations at which aggregate restructuring takes place, the catalytic effect of CR increases, and it decreases again at higher surfactant concentrations in the solution.

Raising the polymer concentration leads to an increase in the apparent rate constant of APEI phosphorylation (Fig. 5a) both in the APEI–AD-16 system (system 1) and in the APEI–AD-16–CR-2 system (system 2). However, the catalytic activity of both systems (Fig. 5b) and the contribution from the calix-

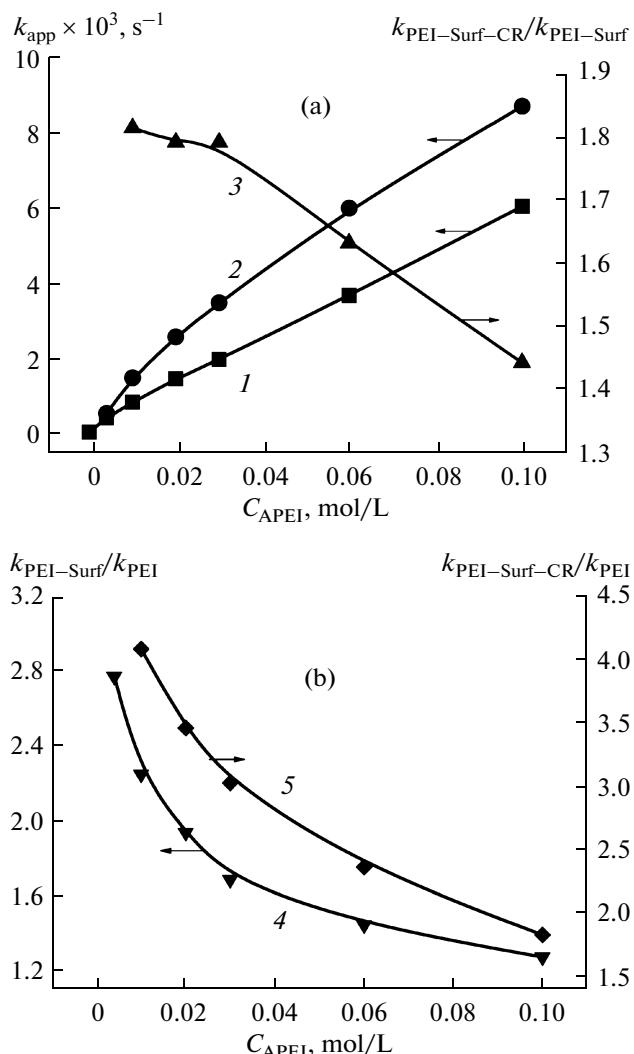
arene to the catalytic effect of system 2  $k_{\text{PEI-Surf-CR}}/k_{\text{PEI-Surf}}$ , Fig. 5a) decrease.

Thus, the study of the phosphorylation of alkylated PEI in the solutions of the cationic surfactants with a cyclic or bicyclic head group, in the solutions of the calix[4]resorcinarenes, and in the mixed solutions of these components has demonstrated that the catalytic effect of the individual and mixed systems depends on the structure of their components and on the concentration and relative amounts of the components in the solution. In the individual surfactant solutions, the catalytic action of the aggregates is observed at any surfactant concentration and the strongest catalytic effect is observed for the surfactant whose head group has a 2-hydroxyethyl moiety (OHPB). The catalytic effect of the phosphorus-containing calixarene CR-2 at low concentrations of the macrocycle is weak, accelerating the reaction by a factor of at most 2. At the same time, this calixarene exerts a fairly strong

**Table 6.** Dependence of the catalytic effect of the APEI–AD-16–CR-2 system on the surfactant concentration

$C_{\text{AD-16}}$ , mol/L	$k_{\text{PEI-Surf}}/k_{\text{PEI}}$	$k_{\text{PEI-Surf-CR}}/k_{\text{PEI}}$	$k_{\text{PEI-Surf-CR}}/k_{\text{PEI-CR}}$
0.001	1.1	2.3	1.1
0.005	1.6	2.7	1.4
0.01	1.9	2.9	1.5
0.02	2.2	3.2	1.6
0.04	2.3	4.1	2.0
0.06	2.8	5.1	2.5
0.08	3.5	5.6	2.9
0.1	4.3	6.1	3.1

Note:  $25^\circ\text{C}$ ,  $C_{\text{APEI}} = 0.01 \text{ mol/L}$ ,  $C_{\text{CR}} = 0.002 \text{ mol/L}$ .



**Fig. 5.** (a) Apparent rate constant of the reaction between APEI and PNCP in chloroform in systems (1) and (2) and (3) the contribution from the calixarene to the catalytic effect of system 2 as a function of the APEI concentration ( $C_{Surf} = 0.04$  mol/L,  $C_{CR-2} = 0.002$  mol/L, 25°C). (b) Dependence of the catalytic effect of systems (4) and (5) on the APEI concentration ( $C_{Surf} = 0.04$  mol/L,  $C_{CR} = 0.002$  mol/L, 25°C).

inhibiting effect, reducing the reaction rate by a factor of ~20, at APEI-to-CR concentration ratios smaller than 2 : 1. In the cationic surfactant + CR-2 mixed solutions (system 2), the calixarene enhances the catalytic effect of the system and the greatest contribution from the macrocycle to the acceleration of the process is observed at low AD-16 and polymer concentrations.

#### ACKNOWLEDGMENTS

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