A novel supramolecular catalytic system based on amphiphilic triphenylphosphonium bromide for the hydrolysis of phosphorus acid esters

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HIGHLIGHTS

- Alkyltriphenylphosphonium bromides form micelles with higher solubilizing capacity.
- The acceleration of the reaction (more than two orders of magnitude) was observed.
- Catalysis is due to the concentration of the reagents in micellar pseudophase.

GRAPHICAL ABSTRACT
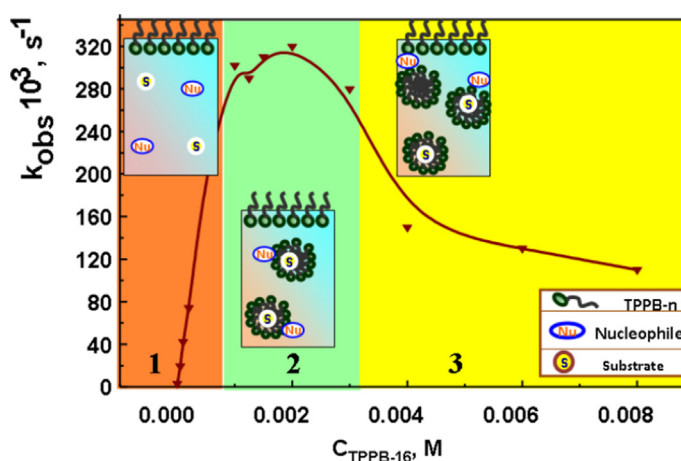
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ABSTRACT

The biomimetic nature of micellar catalysis can significantly affect the rate of chemical reactions due to the effects of concentration and the change of microenvironment. Here, a key role is played by the nature of the head group. The catalytic activity of alkyltriphenylphosphonium bromides (TPPB-n; n = 10, 12, 14, 16, 18; n is the number of carbon atoms in alkyl groups) in the nucleophilic substitution of p-nitrophenyl esters of alkylchloromethylphosphonic acid were investigated by the method of spectrophotometry. Using pyrene, prodan and Sudan I as probes the values of critical micelle concentrations and aggregation numbers were determined. A comparison of the results of kinetic dependence processing by Berezin equation obtained for TPPB series with the known ammonium analogues was carried out. It was found that for TPPB-n series, the higher acceleration of reaction has been achieved due to concentration factor compared to ammonium surfactants. This agrees with the fact that alkyltriphenylphosphonium bromides demonstrate higher aggregation activity forming micelles with higher solubilizing capacity.

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1. Introduction

The 'bottom-up' principle of transition from simple to complicated structures underlying the self-organization of amphiphilic molecules is characteristic of all biological (natural) objects [1–4]. Therefore, surfactants forming supramolecular aggregates of various structures at a particular concentration in their solution are the subject of continuous research interest. The structure of the head group plays an important role in the self-association and catalytic activity of the ionic surfactants [3,4]. In particular, the nature of a head group can substantially influence the nucleophilic substitution with an ionic reagent, since the anionic nucleophile/cationic head group interaction is assumed to determine the effect of the concentration, which plays the key role in micellar catalysis. Despite the fact that the influence of charged fragments on the properties of cationic surfactants (aggregation, solubilization, catalytic activity) has been investigated for a long time, the majority of fundamental studies is represented by alkyltrimethylammonium and alkylpyridinium halides [3,5–15]. Analysis of the data published shows that the number of publications devoted to the effect of the head group structure of cationic surfactants on aggregation and catalysis is mainly related to the variation in the length of alkyl residual and substituents at nitrogen atom [10–12]. Meanwhile the change of charged center of surfactants, e.g. the transition from nitrogen to phosphorus can significantly affect their properties. Our attention was drawn to alkyltriphenylphosphonium bromides due to the following features: (i) lipophilic triphenylphosphonium cation is capable of delivering antioxidants [16–20], dendrimers [21], coenzyme Q10 [22] and other bioactive compounds into mitochondria; these molecules rapidly permeate lipid bilayers and, because of the large mitochondrial membrane potential (negative inside), they can accumulate by a factor of hundreds inside mitochondria [16,17]; (ii) these surfactants have a high solubilizing capacity coupled with a low critical micelle concentration (cmc) as compared with the known ammonium analogues [23,24].

The self-organization of alkyltriphenylphosphonium bromides in water has been investigated in individual solutions [9,23–25], binary [9,26,27] and ternary combinations [28] of TPPB-*n* with alkyl chains bearing 10, 12, 14, and 16 carbons by the methods of conductometry, tensiometry, fluorimetry, viscosimetry, NMR, calorimetry. Furthermore, the micellization behavior of TPPB-*n* in mixed compositions with cationic [24,29] and nonionic surfactants [30], triblock polymers [31], polyethylene glycol [32] has been studied. It was shown specific behavior of this type of surfactants, resulting in low values of cmc and aggregation number [23,24], and high fluorescence quenching [28]. The aggregation of TPPB-*n* in two different room-temperature ionic liquids [33] and in water + ethylene glycol and water + diethylene glycol mixtures (0–30% v/v) has been investigated as well [34].

On the other hand, there are only a limited number of publications on catalytic activity of TPPB-*n* in different types of reaction, despite the fact that the biomimetic nature of micellar catalysis allows us to achieve the reaction acceleration up to several orders of magnitude [1,4,6,7]. Mohareb et al. [35] have studied the effect of TPPB-*n* on the reaction between 4-nitrophenylbenzylsulfonate and bromide ion. It was noted that the rate of the reaction under study is from 3 to 8 times higher in the case of TPPB-*n* as compared to other cationic surfactants. It was also shown that the hexadecyl derivatives of TPPB affect the cleavage of esters [36]. Kinetic experiments have also been done to determine the dependence of observed rate constant for the nucleophilic substitution of *p*-nitrophenyl acetate and benzohydroxamate ions in the presence of cetyltriphenylphosphonium bromide in water + ethylene glycol and water + diethylene glycol mixtures (0–50% v/v) at pH 7.9 and 300 K [34]. Catalytic activity toward phosphonates hydrolysis of

mixed cetyltriphenylphosphonium bromide–polyethylene glycol systems had been studied in Ref. [32].

In order to extend the information database related to the effect of the nature of the surfactant head group on its catalytic properties, additional studies are necessary. In present work, we have studied catalytic and solubilization activity of alkyltriphenylphosphonium bromides series (TPPB-*n*; *n* = 10, 12, 14, 16, 18; here *n* is the number of carbon atoms in alkyl groups, Scheme 1). The main emphasis was laid on the determination of the catalytic effect of the above series on nucleophilic substitution in phosphorus acid esters and the processing of the kinetic dependences within the framework of pseudophase model of micellar catalysis.

2. Experimental

2.1. Chemicals

The synthesis of TPPB-*n* was described in [23]. Pyrene, 1-phenylazo-2-naphthol (Sudan I), *N,N*-dimethyl-6-propionyl-2-naphthylamine (prodan), and cetylpyridinium bromide (CPB) were supplied by Sigma–Aldrich. Ultrapure water (type I, 18.2 MΩ cm resistivity at 25 °C) obtained from the Direct-Q 5 water purification system (with UV lamp) was used for all the solution preparation.

2.2. Fluorescence spectroscopy

The fluorescence spectra of pyrene (1×10^{-6} mol L^{-1}) and prodan (5×10^{-6} mol L^{-1}) in amphiphile solutions were recorded at 25 °C in a Varian Cary Eclipse spectrofluorimeter. Sample excitation was at a wavelength of 335 nm for pyrene and 360 nm for prodan. Emission spectra were recorded within 350–500 nm (pyrene) and 350–650 nm (prodan) ranges. The thickness of the cell was 10×10 mm. Fluorescence intensities of the first peak at 373 nm (I_I) and of the third peak at 384 nm (I_{III}) of pyrene were obtained from the spectra [37]. To measure cmc using prodan, one assumes that any shifting of the fluorescence maximum wavelength arises from dye molecules experiencing different microenvironmental conditions. This different environment is presumed to be due to the micelle formation [38]. The data were analyzed using the Microsoft Excel and Origin Pro 8.5 software.

The aggregation numbers (N_{agg}) were determined by the spectrofluorometric technique using cetylpyridinium bromide(1×10^{-3} M stock solution) as a quencher [39,40]. The main peak (λ394.5 nm) height has been taken for calculation.

N_{agg} were determined according to Eq. (1):

$$\ln \left(I_o / I \right) = -\frac{[Q]}{[Mic]} \tag{1}$$

where I and I_0 represent fluorescence intensities in the presence and in the absence of quencher, respectively, [Q] is quencher concentration, and [Mic] is concentration of the micelles. The N_{agg} values were determined as $N_{agg} = [Mic]/[D]$, where $D = D_t$-cmc is the concentration of micellized surfactant.

2.3. Absorption spectroscopy

Solutions containing an excess of crystalline dye, Sudan I, were allowed to equilibrate for about two days at room temperature. Then they were filtered, and their absorbance was measured at 495 nm (molar extinction coefficient 8700 L mol^{-1} cm^{-1}). Quartz cuvettes with a cell length of 0.5 and 0.1 cm were used.

2.4. Kinetic study

The reaction was controlled by monitoring the *p*-nitrophenolate anion absorption at 400 nm on "Specord 250 Plus" spectropho-
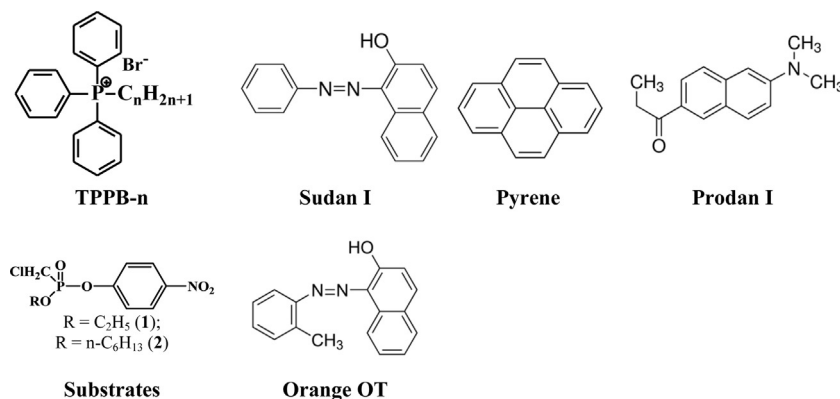
Scheme 1. Formulas of the compound used.

Table 1
The cmc and aggregation number values derived from the fluorescence and the dye solubilization study.

Surfactant	cmc, mM		
	Pyrene fluorescence	Sudan I solubilization	Aggregation number
TPPB-12	1.8	1.2	11 (7 mM)
TPPB-14	0.38	0.33	6 (5 mM)
TPPB-16	0.18	0.16	2 (0.3 mM)
			7 (1 mM)

tometer with temperature-controlled cell. The initial substrate concentration was in the range of 5×10^{-5} to 1×10^{-4} mol L^{-1}. The latter was achieved by the introduction of 2–10 μL of a phosphonate solution in ethanol (0.02 mol L^{-1}) into quartz cells (thickness 0.5 cm or 1.0 cm) containing a solution of surfactant. The observed rate constants (k_{obs}) were determined from the equation: $\ln (A_\infty - A) = - k_{obs} \, t + const$, where A and A_∞ are the absorbance of the micellar solutions at point t during and after completion of the reaction, respectively. The k_{obs} values were calculated using the weighed least-squares computing methods. Each value of k_{obs} is the average of at least three independent determinations differing by no more than 4%.

3. Results and discussion

3.1. Fluorescence data

Fluorescent tags are often used to study the properties of supramolecular systems, since they allow to obtain such information as the values of cmc, the polarity of the microenvironment and the aggregation number at small quantities of substances administered [37,39,40]. The formula for calculating of aggregation number includes concentration of the micelles, so in the early stages of investigation the cmc values were determined by fluorescence spectroscopy. The ratio of intensities of the first and third vibronic peaks of fluorescence emission spectra of pyrene decreases with an increase in the surfactant concentration due to a decrease in the polarity of the microenvironment. Therefore, the sharp change in the I_1/I_3 ratio allows obtaining cmc values. An example of the spectrum of pyrene fluorescence quenching by adding TPPB-16 and dependence of I_1/I_3 ratio on surfactant concentration are shown in Figs. 1 and 2, respectively. The cmc value for dependencies with sigmoid profile is the center of the sigmoid [41]. Such dependence for TPPB-14 and TPPB-12 are given in Supplementary data (Figs. S1 and S3). The cmc values obtained from these plots (Figs. 2, S2, S4) are summarized in Table 1 and are in good agreement with those obtained earlier by other methods [23].
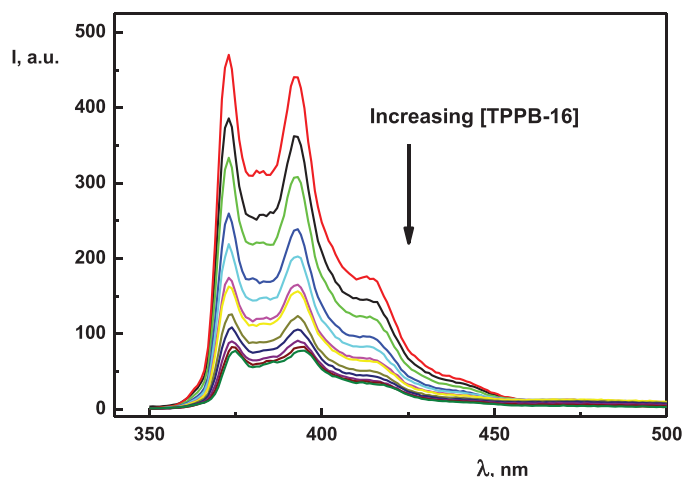

Fig. 1. Fluorescence spectra of 1 μM pyrene in the presence of TPPB-16; 25 °C ($\lambda_{excitation}$ = 335 nm, excitation and emission slits are 5 and 5 nm, respectively). Arrow indicates an increase in the TPPB-16 concentration from 0 (for pyrene alone, red line) to 3×10^{-3} M.
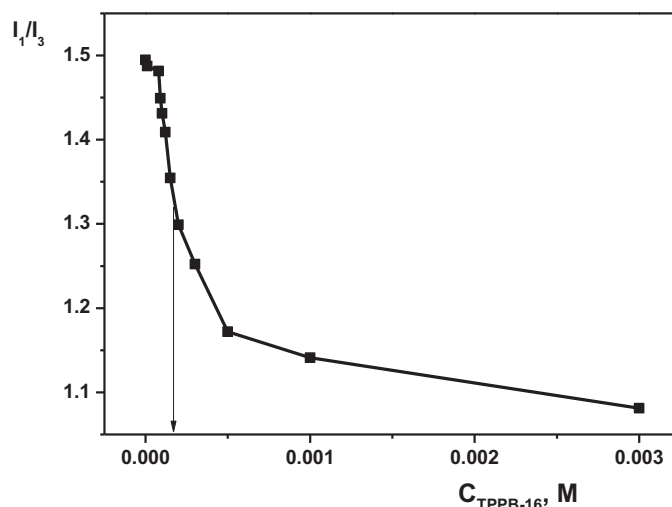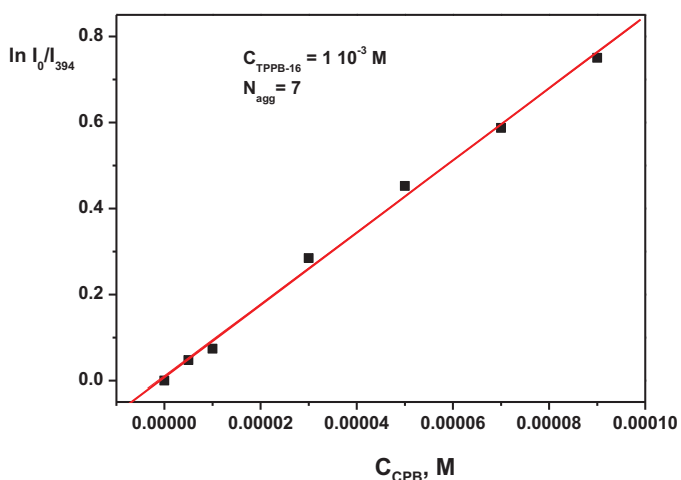

Fig. 2. The ratio of fluorescence intensity of the first vibronic peaks (373 nm) and third vibronic peaks (383 nm) of pyrene in the presence of TPPB-16 vs concentration; 25 °C; C(Py) = 1×10^{-6} M, H$_2$O. The fluorescence spectrum is shown in Fig. 1.

Using of cetylpyridinium bromide (CPB) as a quencher allowed calculating the aggregation numbers exemplified by two concentrations of TPPB-16 0.3 mM (Figs. S5 and S6) and 1 mM (Figs. 3 and 4). At low TPPB-16 concentration (0.3 mM), which is
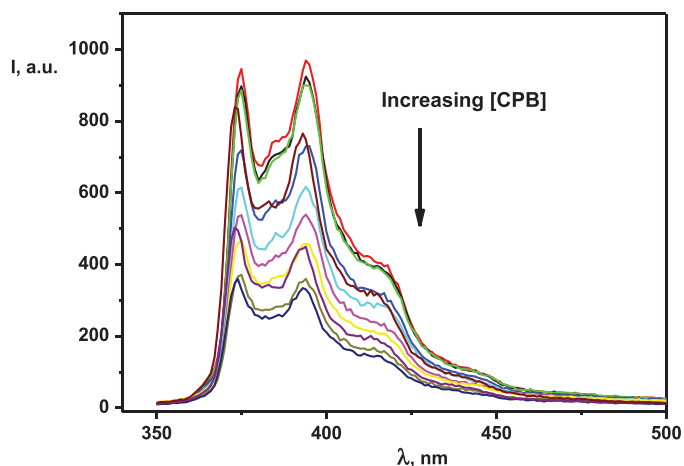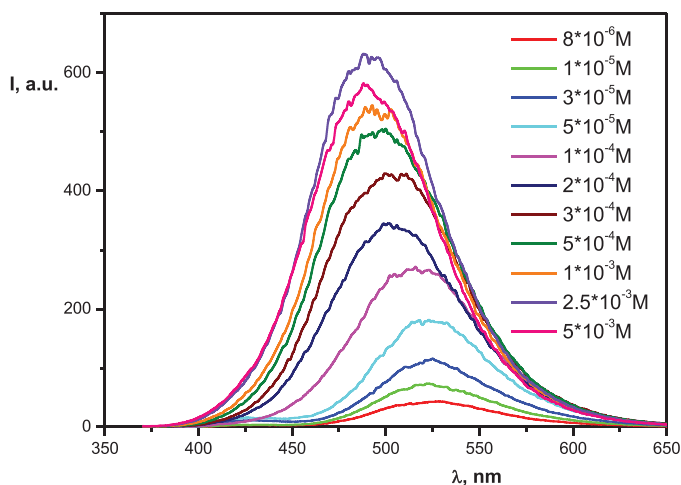
Fig. 3. The quenching of pyrene fluorescence by cetylpyridinium bromide (CPB) in presence of 1×10^{-3} M TPPB-16. Fluorescence spectra recorded for pyrene alone (red line) and cetylpyridinium bromide added in increasing concentrations from 5×10^{-6} M to 7×10^{-4} M. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
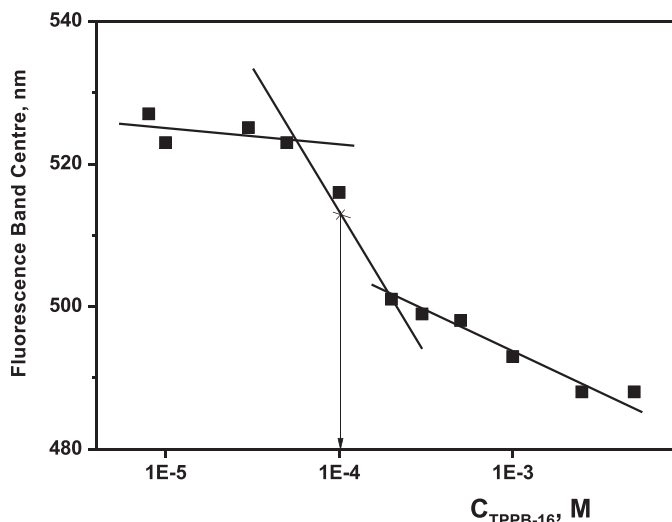

Fig. 5. Fluorescence spectra of 1.6 μM prodan in the presence of increasing concentration of TPPB-16; 25 °C; H_2O ($\lambda_{excitation} = 360$ nm, excitation and emission slits are 2.5 and 5 nm, respectively).


Fig. 4. The ratio of fluorescence intensity of pyrene vibronic peak at 3 9 4 nm in the absence and the presence of cetylpyridinium bromide vs quencher concentration; 25 °C; C(Py) = 1×10^{-6} M; C(TPPB-16) = 1×10^{-3} M; H_2O. The fluorescence spectrum is shown in Fig. 3.

Fig. 6. Plot of the wavelength for maximum prodan fluorescence intensity vs TPPB-16 concentration.

very close to the value of the cmc (0.18 mM), the aggregation number is 2, indicating the formation of premicellar aggregates, viz dimers. Increasing the surfactant concentration up to 1 mM (five-fold exceeds the cmc value) results in the formation of micellar aggregates with aggregation number equal to 7. For cetyltrimethylammonium bromide (CTAB) at the concentration of 3 mM (three times higher compared to cmc) aggregation number, determined by us under the same conditions (Figs. S7 and S8), is equal to 37. Such low number of aggregation compared to ammonium surfactant can be explained by the structure of the bulk head group and inability to include of a large number of monomers in the aggregates. The value of aggregation number is also affected by the length of the alkyl radical of phosphonium surfactants: for TPPB-14 at concentration of 5 mM aggregation number equals 6 (Figs. S9 and S10, Table 1), and for TPPB-12 at a concentration of 7 mM it equals 11 (Figs. S11 and S12, Table 1). It was shown using TPPB-14 as an example that more than tenfold concentration excess as compared to cmc value does not lead to a large increase in the numbers of aggregation.

To determine the cmc value of TPPB-16 another fluorescent probe, prodan, was also used. Solvatochromic shift of prodan is very useful for determining the cmc of surfactants; when the probe pass from aqueous solution to micellar medium the polarity of the microenvironment dramatically changes, which causes the shift of the maximum on fluorescence spectrum (Fig. 5). The dependence of the fluorescence band centre on surfactant concentration gives a break point corresponding to the cmc (Fig. 6).

3.2. Solubilization of Sudan I data

Solubilization of dyes in micelles is an important property of surfactants. In addition, the solubilization phenomenon allows determining the cmc in water and in non-aqueous solutions. The method is based on two observations: (1) at a concentration below the cmc solution hardly solubilized dye; (2) when it reaches the concentration corresponding to cmc, the solubility of the dye increases sharply [42,43]. Colloidal dissolution or solubilization occurs in the hydrophobic core of the micelles (aggregates). For the experiment, Sudan I (Scheme 1) was used that has an absorption band in the visible spectrum at 495 nm. The concentration dependences of the optical density are shown in Figs. 7 , S13, S14.
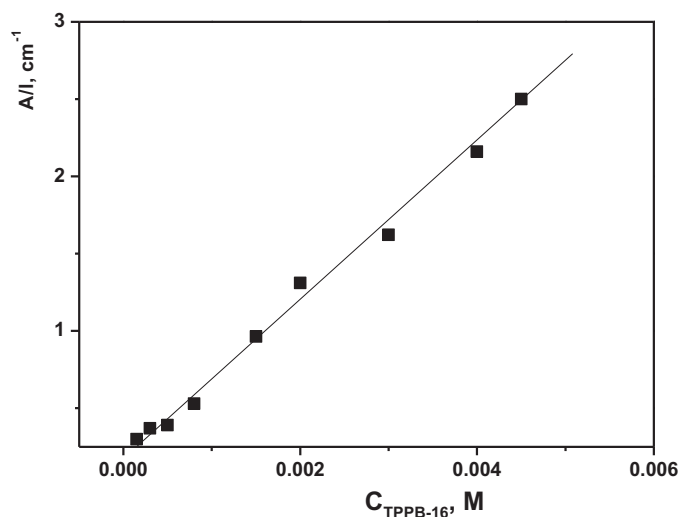
Fig. 7. Dependence of optical density at 495 nm reduced to 1 cm path of TPPB-16 solutions on the surfactant concentration; 25 °C.

Table 2
The dependence of dye solubilization data (slope parameter b and solubilization power S) on number of carbon atoms in alkyl chain.

n	Sudan I		Orange OT[a]	
	b	$S \times 10^3$	b	$S \times 10^3$
12	257	29.54	233	13.4
14	375	43.10	348	20.0
16	473	54.37	482	27.7

[a] Our data published in [23].

Based on the analysis of spectrophotometric data the amount of dye solubilized by the micelles can be calculated from Eq. (2):

$$S = b/\epsilon, \tag{2}$$

where b is the slope of the linear range of the dependences shown in Figs. 7, S13, S14, ϵ is the extinction coefficient of the Sudan I ($8700 \, \mathrm{L \, mol^{-1} \, cm^{-1}}$), S is the solubilizing power, i.e., the number of moles of solubilized dyes per moles of micellized surfactants.

Table 2 summarizes values of the slope parameter b and the solubilization power S. It is shown that the solubilization capacity of TPPB-n expectedly increases with increasing length of the alkyl chain. It is interesting to note that the comparison of the results obtained previously for solubilization of the other dye [23], Orange OT showed that despite a slight difference in the structure of these dyes, the solubilizing power of surfactants under study toward Sudan I is higher by two times.

3.3. Catalytic activity

As amphiphiles form micelles with a hydrophobic core and a polar shell in aqueous solutions after reaching critical micelle concentration, they have active centers for binding both hydrophobic and hydrophilic reagents. This feature has been successfully used for the catalysis of different types of reactions including the nucleophilic substitution [3,4,8,10–12]. The mechanism of micellar catalysis is compared with the effect of enzymes. The latter have hydrophobic regions in the active centers in which the orientation of reagents and increasing their local concentration are provided. Reactions catalyzed by micelles are usually treated in terms of pseudophase model as proposed by previous researchers [44–46]. According to this model the substrate is distributed between the bulk aqueous phase and the micellar pseudophase. The reaction

usually proceeds in both phases and the total reaction rate is a combination of the rates in each phase.

It is known that the transfer of the phosphoryl group is an important step in the processes taking part in living organism; therefore alkyltriphenylphosphonium bromides were tested as catalysts in the nucleophilic substitution of p-nitrophenyl esters of alkylchloromethylphosphonic acid (Scheme 2), with the hydrophobicity of amphiphilic compound and substrate varied. The series of trimethylammonium bromides (TMAB) was studied under the same conditions for determining of head group role.

The kinetic dependences of phosphonates hydrolysis in the presence of the surfactants proceed through a maximum (Figs. 8 and 9). It should be noted that the maximum on kinetic curves is shifted towards the lower concentrations with the increase in the hydrophobicity of substrate. The latter suggests the evidence of the more effective binding of hexyl substituted substrate with the hydrophobic micellar core.

The treatment of kinetic dependences by means of pseudophase model of micellar catalysis was performed according to Eq. (3) [44]:

$$k_{\mathrm{obs}} = \frac{k_{2,0} + (k_{2,\mathrm{m}}/V)K_S K_{Nu} C_{\mathrm{surf}}}{(1 + K_S C_{\mathrm{surf}})(1 + K_{Nu} C_{\mathrm{surf}})} \tag{3}$$

where k_{obs} ($\mathrm{L \, mol^{-1} \, min^{-1}}$) is observed second-order rate constant when divided of observed rate constant by the concentration of nucleophile; $k_{2,0}$ and $k_{2,\mathrm{m}}$ ($\mathrm{L \, mol^{-1} \, min^{-1}}$) are second-order rate constants in bulk and micellar phase, respectively; V ($\mathrm{L \, mol^{-1}}$) is molar volume of surfactant; K_S and K_{Nu} ($\mathrm{L \, mol^{-1}}$) are binding constants of substrate and nucleophile respectively; and C_{surf} ($\mathrm{mol \, L^{-1}}$) is concentration of surfactant in solution minus critical micelle concentration.

According to the Berezin model [44], maximum rate acceleration is described by Eq. (4), which is a modification of Eq. (3):

$$\left(k_{\mathrm{obs}}/k_{2,0}\right)_{\max} = \frac{k_{2,\mathrm{m}}}{k_{2,0}} \times \frac{K_S K_{Nu}}{V \left(K_S^{1/2} + K_{Nu}^{1/2}\right)^2} \tag{4}$$

The first factor in the right part of Eq. (4) reflects the change of microenvironment of reagents when passing from the solvent into micellar phase (F_{m}) and the second describes effect of concentration of reagents in the aggregates (F_c). After aggregates had formed in solution, the main part of reagents is transferred from aqueous phase to micelles. The volume of micellar phase is relatively small; therefore, sharp increase of local concentrations of the reagents occurs. Another factor of micellar catalysis, i.e. factor of microenvironment, changes as well. The microscopic properties of medium such as dielectric constant and microviscosity can remarkably change, thereby affecting the reaction rate, when the transition from volume phase to micellar pseudophase occurs.

The dependence with maximum can be explained from two complementary viewpoints. On the one hand, the sharp increase in the rate constant might be due to the strong binding of substrate with micelles. This brings about the transfer of substrate into aggregates at low concentration of surfactant. Further increase in concentration of amphiphilic compound results in the growth in the number of micelles and, therefore, dilution of reagents (low constant rate). Another explanation follows from the theory of ionic exchange in the Stern layer between surfactant counterions and hydroxide ions. At low surfactant concentration the amount of solubilized substrate and hydroxide ions in the Stern layer sharply increases; this leads to increase of rate constant. The increasing in the concentration of surfactant brings about the increase in the number of bromide ions, which displaces hydroxide ions from the surface layer of micelles.

The processing of kinetic dependences (Figs. 8 and 9) by means of pseudophase model of micellar catalysis according to Eqs. (3) and (4) allowed us to obtain the following numerical data of the bind-

R = Et (1), n-C_6H_{13} (2)
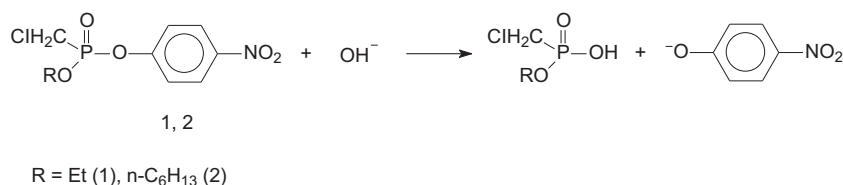
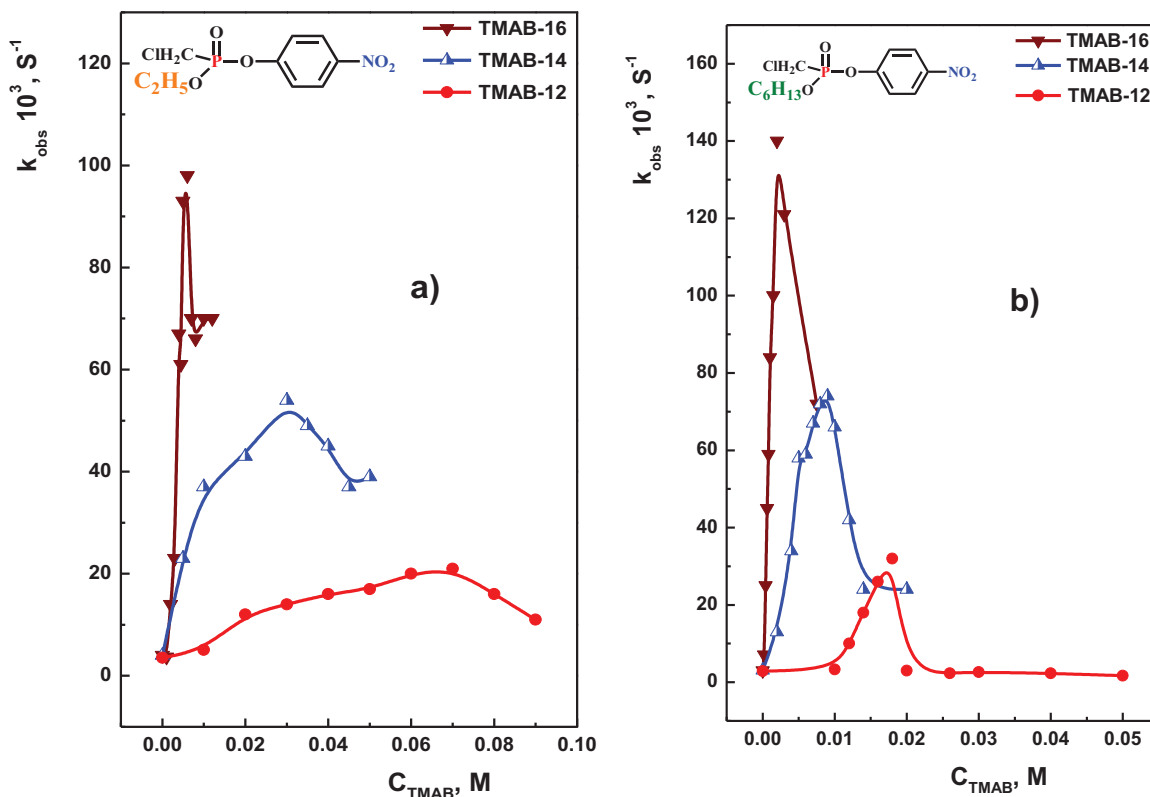**Scheme 2.** The reaction of alkali hydrolysis of the substrates **1** and **2**, 0.001 MNaOH, 25 °C.
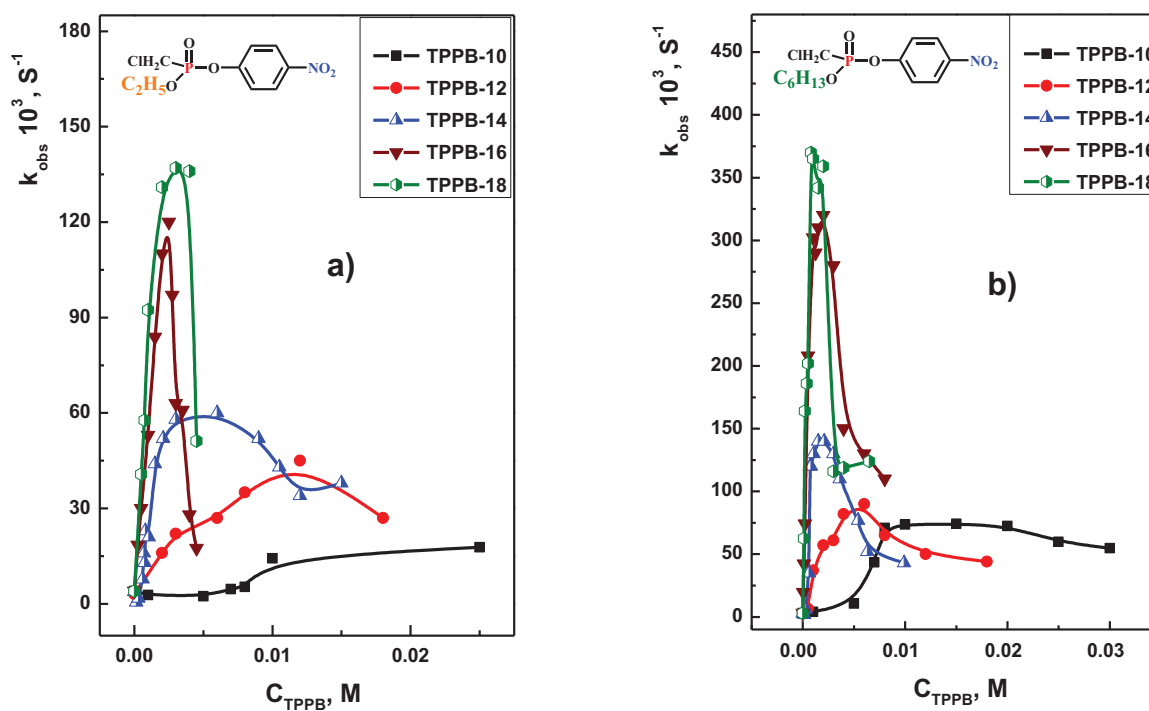
Fig. 8. The observed rate constant of alkali hydrolysis of substrates **1** (a) and **2** (b) in individual solution of TPPB-*n* vs concentration of amphiphilic compound, 0.001 MNaOH, 25 °C.

Table 3
The parameters of alkali hydrolysis of substrates **1** and **2** in TPPB-*n* solutions calculated according to Eq. (4).

Surfactant	$k_{2,m}$ (L mol^{-1} min^{-1})	K_S (L mol^{-1})	K_{Nu} (L mol^{-1})	F_m	F_c	$F_m \times F_c$	k_{max}/k_0	cmc, mM
O-ethyl-*O*-*p*-Nitrophenylchloromethylphosphonate (substrate **1**)								
TPPB-18	0.315	2986	168	0.0786	366	29	34	0.43
TPPB-16	0.373	1630	146	0.0933	288	27	30	0.2
TPPB-14	0.278	1504	96	0.0694	203	14	15	1.2
TPPB-12	0.588	433	30	0.1471	63	9	11	2.3
TPPB-10	0.575	373	18	0.1437	41	6	4.5	9.1
O-hexyl-*O*-*p*-Nitrophenylchloromethylphosphonate (substrate **2**)								
TPPB-18	0.562	5040	315	0.1873	672	126	122	0.08
TPPB-16	0.476	3991	281	0.1587	585	93	107	1.6
TPPB-14	0.415	1389	205	0.1384	340	47	47	0.84
TPPB-12	0.357	630	180	0.1190	255	30	30	1.6
TPPB-10	0.612	434	75	0.204	125	25.5	25	7.2

Table 4
The parameters of alkali hydrolysis of substrates **1** and **2** in TMAB-*n* solutions calculated according to Eq. (4).

Surfactant	$k_{2,m}$ (L mol^{-1} min^{-1})	K_S (L mol^{-1})	K_{Nu} (L mol^{-1})	F_m	F_c	$F_m \times F_c$	k_{max}/k_0	cmc, mM
O-ethyl-*O*-*p*-nitrophenylchloromethylphosphonate (substrate **1**)								
TMAB-16	0.1887	2219	301	0.0472	536	25	24.5	3.85
TMAB-14	0.5882	623	46	0.1471	94	14	13.5	19.3
TMAB-12	0.463	318	30	0.1157	58	7	5	54
O-hexyl-*O*-*p*-nitrophenylchloromethylphosphonate (substrate **2**)								
TMAB-16	0.2427	2302	290	0.0809	526	46	47	0.85
TMAB-14	0.3667	1621	70	0.1244	160	20	25	3.78
TMAB-12	0.4	495	45	0.1344	89	11	12	13.5

Fig. 9. The observed rate constant of alkali hydrolysis of substrates 1 (a) and 2 (b) in individual solution of TMAB-*n* vs concentration of amphiphilic compound, 0.001 MNaOH, 25 °C.

ing constant of reagents with aggregates, rate constants in micellar pseudophase, and rate acceleration (Tables 3 and 4). According to the data given in the tables, change of microenvironment of the reagents due to the transition of reaction into surfactant aggregates affects adversely the process. In all cases, F_m value is less than one. Due to the rather high values of F_c the unfavorable action of the first factor is compensated and there appears the catalytic effect up to 122 times in the case of TPPB-18.

Comparison of the results obtained for TPPB-series with known ammonium counterparts was performed (Tables 3 and 4). It was determined that higher values of acceleration for TPPB-*n* achieved owing to factor of concentration can be related to high aggregation activity of TPPB-*n* providing the formation of bulky micelles with higher solubilization ability.

It was found that a series of TPPB-*n* is able to exhibit remarkable substrate specificity in alkali hydrolysis of phosphonates. For example, transition from less hydrophobic substrate **1** to more hydrophobic **2** results in the significant increase of the factor of reagents concentration. The dependence of F_c on the number of carbon atoms in alkyl chain of TPPB-*n* (Fig. S15,a) is described by Eqs. (5) and (6) for substrates **1** and **2**, respectively:

$$F_c = 43.75n - 420, \tag{5}$$

$$F_c = 71.2n - 601.4. \tag{6}$$

This can confirm the stronger interaction of higher homologues of TPPB-*n* with hydrophobic substrate. For this reason, more sharp growth in the factor of concentration is observed on the transition from TPPB-10 to TPPB-18 compared to substrate **1**. Hydrophobic reagent can presumably concentrate not only in hydrocarbon region of micelles, but also in the range of three phenyl rings of TPPB-*n*; this would be the reason of different values of factor of reagent concentration. In the case of TMAB series, factor of concentration did not change remarkably at the variation

of hydrophobicity of substrate, and binding of nucleophile and reagents with TMAB-16 aggregates was almost identical for both substrates (Fig. S15,b).

4. Conclusions

This study focuses on the elucidation of the role of head group of cationic surfactants. In particular, aggregation capacity, solubilization power and catalytic effect are compared for two homological series of cationic surfactants bearing phosphonium and ammonium charged fragments. While TMA series is well studied, little information is available about phosphonium surfactants, with some contradictory observed in respect of aggregation number of micelles formed. Triphenylphosphonium salts are shown to have significantly lower values of cmc as compared with ammonium analogs. This paper gives at the first time systematic data on catalytic activity of TPPB micelles toward hydrolytic decomposition of organophosphorus ecotoxicants and factors responsible for the micellar rate effect. Importantly, higher acceleration of the reaction is observed for phosphonium series compared to ammonium analogs, which is in good agreement with their superior aggregation and solubilization properties. Parameters of micellar catalysis within the framework of pseudophase model were calculated using mathematical models and original program. The acceleration of the reaction (more than two orders of magnitude) due to the concentration of the reagents in micellar pseudophase was proved.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.colsurfa.2015.10.032.

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