Colloids and Surfaces A: Physicochem. Eng. Aspects 419 (2013) 186–193

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Novel self-assembling systems based on amphiphilic phosphonium salt and polyethylene glycol. Kinetic arguments for synergetic aggregation behavior

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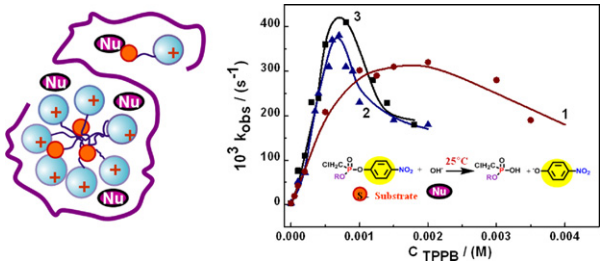
HIGHLIGHTS

- Synergetic behavior occurs in the phosphonium surfactant–PEG systems.
- Zeta-potential of cationic micelles decreases in the presence of PEG.
- The counterion binding of micelles decreases with the addition of PEG.
- An increase in the reactivity of phosphonates occurs in polymer-bound micelles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 September 2012
Received in revised form
26 November 2012
Accepted 29 November 2012
Available online xxx

Keywords:
Polyethylene glycol
Cetyl triphenyl phosphonium bromide
Aggregation
Kinetics
Phosphorus acid esters

ABSTRACT

Structural behavior and catalytic activity toward basic hydrolysis of O-alkyl-O-p-nitrophenyl chloromethyl phosphonates (alkyl = ethyl (S1) and hexyl (S2)) of mixed cetyl triphenyl phosphonium bromide (TPPB)–polyethylene glycol (PEG) systems are studied. The interdependence of aggregates and substrates is revealed from symbate changes in their self-diffusion coefficients determined by NMR FT-PGSE method. Much lower zeta-potentials of mixed systems as compared to single TPPB micelles are found, although the counterion binding of aggregates decreases with the addition of PEG. A 1.5–2-fold increase in the reactivity of phosphonates is shown to occur in mixed TPPB–PEG systems versus single surfactant micelles. In addition, a polymer induced shift of the onset of the rate acceleration toward the lower concentrations is observed. These findings provide strong evidences for synergetic solution behavior in the TPPB–PEG systems. The quantitative treatment of kinetic data in terms of pseudophase model sheds light on the factors of catalytic action. In the case of hydrolysis of S1, the more favorable microenvironment is responsible for the higher catalytic effect of mixed systems as compared to single TPPB micelles, while the factor of concentration decreases. The opposite trend is observed for hydrolysis of phosphonate S2, for which an increase in the micellar rate effect with the PEG addition is mainly contributed by the growth of the factor of concentration.

1. Introduction

The catalysis of reactions in organized media is of current interest [1–8]. Effects of single micellar solutions and microemulsions on reaction rates have been extensively studied [1–4]. In these systems, aggregates act as nano- or microreactors, compartmentalizing and concentrating or diluting reagents and thereby altering the observed rate of chemical reactions. The sphere of our interest is the design of supramolecular catalytic systems for reactions of nucleophilic substitution in phosphorus and carbon acids [9–12]. These reactions are of significance in organic chemistry and play a key role in biology [13]. Cationic micelles are known to accelerate these reactions due to effective

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http://dx.doi.org/10.1016/j.colsurfa.2012.11.071

binding of negatively charged nucleophiles (concentration factor) and change of the microenvironment of reagents (microenvironmental factor). Meanwhile, self-organization and catalytic activity of organized systems may be modified by the addition of polymers. In this case synergetic effect may be observed, such as lowering the critical micelle concentration (cmc), an increase in the catalytic activity, etc. [11,14]. The solution behavior of the uncharged polymer/anionic surfactant systems is well documented [14–17]. In the case of cationic surfactants only their complexes with polyanions have been intensively studied [18–22], while interactions with uncharged polymers have been scarcely explored [23–26]. Unlike the single surfactant solutions, the design of polymer–surfactant catalytic systems is a relatively novel field covered by only isolated works [27–34]. Therefore the investigation of the catalytic activity of cationic surfactant–uncharged polymer mixtures is an urgent problem, being of practical and fundamental importance. It should be noted that the kinetic study may in turn provide arguments in favor of synergetic aggregation behavior in the mixed systems.

Herein, the cationic surfactant cetyl triphenyl phosphonium bromide (TPPB) and the water soluble polymer polyethylene glycol (PEG) were chosen as components for polymer–colloid catalytic systems. Amphiphilic phosphonium salts present an important type of cationic surfactants with improved aggregation and solubilization capacity [35–40]. They are widely used in modern technologies including the drug delivery systems, antimicrobial formulations, antioxidant additives, etc. [41–43]. The catalytic micellar effect of surfactants with phosphonium head groups is exemplified by isolated publications [44–47]. Similarly, the binary TPPB–PEG catalytic system has not previously been studied. Self-assembly of single TPPB solutions is studied in our earlier work [48]. As a chemical reaction, basic hydrolysis of two substrates of different hydrophobicity, O-alkyl-O-p-nitrophenyl chloromethyl phosphonates: alkyl = ethyl (S1); and hexyl (S2) are studied (Fig. 1, Scheme S1).

Phosphorus acid esters are compounds with interesting biological and pharmacological properties and are widely used as pesticides, drugs, and nerve gases [49,50]. The hydrolysis of phosphorus acid esters proceeds through breaking the P—O bond, which is facilitated by the presence of electron-withdrawing groups. Cationic micelles catalyze the reaction due to electrostatic attraction of hydroxide-ions to the oppositely charged head groups, resulting in concentration of the reagents.

2. Experimental

2.1. Materials

Synthesis of TPPB was described elsewhere [48]. Phosphonates S1 and S2 are synthesized according to published procedure [51]. Commercial O-p-nitrophenyl-O,O-diethyl phosphate (S3) and PEGs, average molecular mass of 1000 and 20,000 g mol^{-1} were from "Aldrich". To simplify the analysis of the data, the solution concentrations of PEGs are given as a molar concentration on a monomer basis (moles of monomer per liter of solution). Aqueous solutions were prepared using bidistilled water.

2.2. NMR experiments

All NMR experiments were performed on a Bruker AVANCE-600 spectrometer operating at 600.13 and 242.94 MHz for the ^{1}H and ^{31}P, respectively. The spectrometer was equipped with a Bruker multinuclear *z*-gradient inverse probe head capable of producing gradients with strength of 50 G cm^{-1}. All experiments were carried out at 30 ± 0.2 °C. Chemical shifts were reported relative to HDO (4.7 ppm) and H_3PO_4 (0 ppm) for ^{1}H and ^{31}P, respectively. The Fourier transform pulsed-gradient spin-echo (FT-PGSE) [52–55] experiments were performed by BPP–STE–LED (bipolar pulse pair–stimulated echo–longitudinal eddy current delay) sequence. Data were acquired with a 50.0 or 120.0 ms diffusion delay, with bipolar gradient pulse duration from 2.2 to 6.0 ms (depending on the system under investigation), 1.1 ms spoil gradient pulse (30%) and a 5.0 ms eddy current delay. The bipolar pulse gradient strength was varied incrementally from 0.01 to 0.32 T/m in 16 steps.

The diffusion experiments were performed at least three times and only the data with the correlation coefficients of a natural logarithm of the normalized signal attenuation ($\ln I/I_0$) as a function of the gradient amplitude $b = \gamma^2\delta^2g^2(\Delta - \delta/3)$ (γ is the gyromagnetic ratio, g is the pulsed gradient strength, Δ is the time separation between the pulsed-gradients, δ is the duration of the pulse) higher than 0.999 were included. All separated peaks were analyzed and the average values were presented. The temperature was set and controlled at 30 °C with a 535 l/h airflow rate in order to avoid any temperature fluctuations owing to sample heating during the magnetic field pulse gradients. After Fourier transformation and baseline correction, the diffusion dimension was processed with the Bruker Xwinnmr software package (version 3.5). The pulse programs for all NMR experiments were taken from the Bruker software library. The effective hydrodynamic radius (R_H) was calculated according to the Einstein–Stokes equation: $D_S = k_BT/6\pi\eta R_H$, in which D_S is the diffusion coefficient, k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity. To estimate roughly the aggregation numbers the Connolly solvent-excluded volumes (CSEV) were used; CSEV is the volume contained within the contact molecular surface created when a sphere (representing the solvent) is rolled over the molecular model.

To calculate the substrate binding fraction (P_b) the two-site model for the case of the fast exchange between the bound and unbound state of the guest molecule in the NMR time scale [55] is used

$$P_b = \frac{(D_{G,obs} - D_{G,free})}{(D_{G@sur} - D_{G,free})}$$

where $D_{G,obs}$ is the apparent (weighed average) self-diffusion coefficient of the guest molecule in the micellar solution, $D_{G@sur}$ is the self-diffusion coefficient of the substrate/aggregate species and $D_{G,free}$ is the self-diffusion coefficient of the free guest in the same solvent, $D_{G@sur}$ is assumed to equal D_S of the surfactant. The regime of fast exchange on the diffusion time scale (50 ms in our case) can be justified by the fact, that it is already fast on the chemical shift time scale, since we observe only one set of signals in all cases. The exponential slope of signal intensity in FT-PGSE experiments also confirms this conclusion.

2.3. Electrode potential measurement

An electromotive force with using an ion-selective electrode is well appropriate for measuring the activity of ionic species. The Nernst equation is known to describe the relation between the electrode potential (ΔE) and the activity of bromide ion (a_{Br}):

$$\Delta E = -\frac{RT}{F}\ln(a_{Br}) + \text{const}, \quad (1)$$

where F is the Faraday constant and the ideal slope (RT/F) is 59.2 mV/equiv at 25 °C [56]. The measurements were performed for the counterion (Br^-), using an ion meter I-160MI, with a Br-selective electrode ELIS-131Br and a reference electrode ESr-10101/3.0. The electromotive force (ΔE) of the cell was measured for the sample solutions with a stepwise increasing concentration, in which the temperature of the sample was kept constant at 25 °C. For this cell, the Nernst equation was valid over the concentration

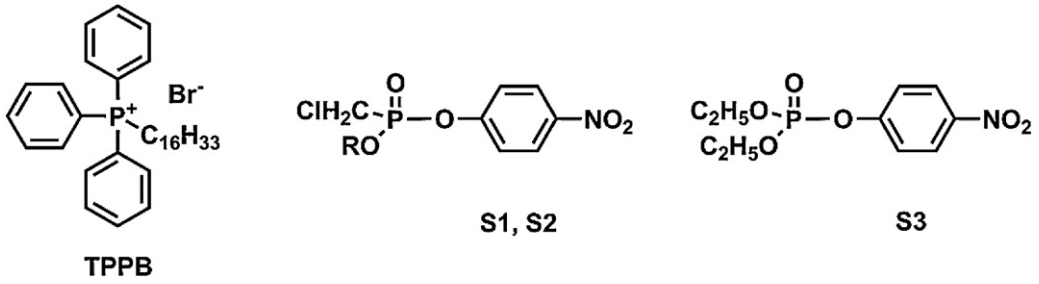

Fig. 1. Structural formulas of cetyl triphenyl phosphonium bromide and substrates:O-alkyl-O-p-nitrophenyl chloromethyl phosphonates; alkyl = ethyl (S1); n-hexyl (S2); O-p-nitrophenyl-O,O-diethyl phosphate (S3).

range from 10^{-6} to 10^{-1} M whenever KBr was used as a solute. Starting from the surfactant concentration of 0.001 M correction factors were used for the calculation of bromide ion concentration from the activity. The degree of counterion binding to aggregates, β, which is the ratio of counterions and amphiphile ions in the micelles, can be calculated from the mass balance for the surfactant ion and the counterion at any total concentration C_t using the following expression:

$$\beta = \frac{(C_t - [Br^-])}{(C_t - \mathrm{cmc})}. \quad (2)$$

2.4. Kinetic study

The second order rate constants of the basic hydrolysis of the substrates S1, S2 and S3 at 25 °C are equal to 4.0, 3.0 and 0.01 M^{-1} s^{-1}. The reaction was controlled by monitoring the p-nitrophenolate-anion absorption at 400 nm. A "Specord M-400" spectrophotometer with temperature-controlled cell holders was employed. All runs were performed at the substrate concentration of 5×10^{-5} M. The observed rate constants (k_{obs}) were determined from the equation: $\ln(A_\infty - A) = -k_{obs}t + \mathrm{const}$, 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 mean of at least three independent determinations differing by no more than 4%.

2.4. The kinetic theory

In our work, the kinetic data were treated in the frame of the theory proposed by Berezin et al. [57]. This model is based on the pseudophase approach and makes it possible to calculate a true rate constant of bimolecular reactions in the micellar phase and the binding constants of reagents and hence to differentiate the factors responsible for the micellar effects. According to this theory, the rate law may be expressed in the following way:

$$k'_{obs} = \frac{k_{2,w} + k_m K_S K_{OH} C}{(1 + K_S C)(1 + K_{OH} C)} \quad (3)$$

where k'_{obs} is the second order rate constant obtained by division of the observed pseudo first rate constant (k_{obs}) by the total nucleophile concentration; $k_{2,w}$ is the second order rate constant of the reaction in the water, k_m (=$k_{2,m}/V$) represents the reactivity in the micellar phase where the reaction occurs; V is the molar volume of micellar pseudophase; C is the total surfactant concentration minus cmc of the surfactant mixture; K_S is the binding constant of substrate (S) related to the partition coefficient $P_S = [S]_m/[S]_w$ in the following way: $k_S = (P_S - 1)V$; indices w and m refer to the water and micellar pseudophase, respectively. As the true bimolecular rate constant for the reaction in the micellar phase $k_{2,m}$ is related to k_m by $k_{2,m} = Vk_m$, to determine the reactivity in the micellar phase one is required to assume a value for the volume of the micellar pseudophase. Value of V for systems based on surfactants and polymers can be calculated based on their molecular weight and density [58,59]. According to the data [57] the apparent molar volumes of single cationic surfactants average 0.3–0.4 M^{-1}. Taking into account the molecular weight of the surfactant and water associated with the polar groups of components, V is estimated to be about 0.9–1.1 L/mol for the title systems. Therefore, in crude approximation the K_S values coincide with partition coefficients P_S.

One of the points for criticism of the classical pseudophase model is associated with the partition of charged species between water and micellar phase. Two alternative approaches have been developed to treat the counterion binding in Stern layer. The widely used pseudophase ion-exchange model takes into account the competition between counterions for a micellar surface, while another approach treats the counterion binding in terms of the surface potential. Both these semi-empirical approaches are not free from limitations [60,61]. Moreover, pseudophase ion-exchange model fails to describe exactly OH binding with cationic micelles. In our earlier work [62] we compared K_{OH} values calculated in terms of Eq. (3) and that obtained by using electrostatic approach, viz. formula: $P_{Nu} = \exp(-e\Psi/kT)$ [63], here k is a Boltzmann constant, and e is an elementary charge. The results of the calculations based on electrostatic model and obtained in the fitting procedure were in a satisfactory agreement, and therefore herein we continue to use Eq. (3) for modeling the kinetics of ion–molecular reaction. Despite the different nature of forces contributing to the binding of substrate and ionic nucleophile with micelles, there is the general physical meaning for constants K_S and K_{OH} derived from fitting procedure with the help of Eq. (3), i.e. the partition of both reagents between two phases.

The approach developed by Berezin makes it possible to differentiate the factors responsible for the micellar effects by using Eq. (4).

$$\left(\frac{k_{obs}}{k_w}\right)_{max} = \frac{k_{2,m}}{k_{2,w}} \times \frac{K_S K_{OH}}{V(\sqrt{K_S} + \sqrt{K_{OH}})^2} \quad (4)$$

The term on the left expressed as the ratio between the pseudo first rate constants in the micellar system and water describes the maximum acceleration of the reaction. The first term on the right is associated with the influence of the micellar microenvironment (F_m) and the second term reflects concentrating the reagents in micelles (F_c).

3. Results and discussion

Micellar catalysis is associated with the formation of aggregates, which can bind reagents thereby changing their local concentrations and microenvironment [57]. Therefore, prior to the reactivity study the aggregation behavior in the system are investigated in both the presence and the absence of substrates. Since phosphonates S1 and S2 are rather reactive and can be hydrolyzed

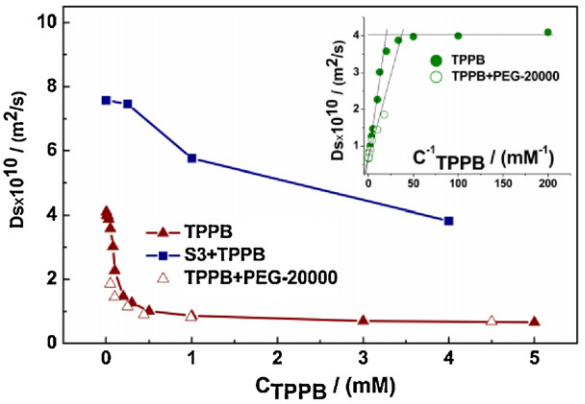

Fig. 2. The dependences of the self-diffusion coefficients of TPPB and substrate S3 on the TPPB concentration in single surfactant system and with the substrate S3 and PEG-20,000 added; Inset shows the dependence of self-diffusion coefficients of TPPB on the inverse concentration; 30 °C.

in the course of experiments, the model low reactive substrate p-nitrophenyl diethyl phosphate (S3; $k_{2,OH} = 0.01\ M^{-1}\ s^{-1}$) is used in the self-assembly study (Fig. 1).

3.1. NMR-self-diffusion study

NMR spectroscopy provides highly effective and precise instrument for elucidation of aggregation behavior of every species in multicomponent systems, since the signal of each component can be monitored. Herein, self-diffusion coefficient (SDC) measurements are invoked to estimate the aggregation parameters, i.e., cmc, hydrodynamic radius, and the number of aggregation as functions of the surfactant concentration, as well as the mutual dependence of components during the aggregation.

NMR data in Fig. 2 show that a marked decrease in SDC of TPPB occurs with an increase in the concentration, which is a forcible argument for the aggregation of the surfactant. The cmc value obtained as a crosspoint in the D_S vs. $1/C$ coordinates (Fig. 2, inset) equals 0.1 mM. The effect of a polymer on the TPPB aggregation is exemplified by PEG-20,000. The addition of the polymer results in a marked decrease of the SDC of TPPB (Fig. 2), which strongly supports the formation of mixed aggregates. Indeed, a ca. twofold decrease in D_S of TPPB occurs at low surfactant concentrations as compared to single TPPB solution (i.e., D_S decreases from 3.58×10^{-10} to $1.86 \times 10^{-10}\ m^2\ s^{-1}$ upon the addition of PEG to the single 0.05 M TPPB solution). The cmc values decreases to the value of 0.03 mM in the mixed TPPB–PEG-20,000 system. Importantly, the addition of the substrate markedly affects the micellization of TPPB within the low concentration range. Thus, in 0.25 mM TPPB solution, D_S of the surfactant decreases from $1.37 \times 10^{-10}\ m^2\ s^{-1}$ (single TPPB solution) to $1.09 \times 10^{-10}\ m^2\ s^{-1}$ in the presence of 1 mM substrate S3, which corresponds to an increase in the number of aggregation from 29 to 53 (Table 1). At higher surfactant concentration this effect becomes negligible due to the increase in the surfactant to substrate ratio.

A marked decrease of the substrate SDC values with increase of the TPPB concentration (Fig. 2) proves substrate binding with micelles. This dependence is due to the S3 is in exchange between the bulk solution and micelles, so that its observed D_S values are weight averaged between the fast (free substrate molecules) and slow (micelle bound substrate) components, with the latter increasing with the surfactant concentration. The weight of the bound substrate (P_b) increases from 3.5% to 55% with an increase in the TPPB concentration from 0.25 mM to 4 mM (Table 1). A marked influence of PEG on the substrate binding is also observed, e.g. a 5-fold increase in P_b is revealed in the binary TPPB–PEG-20,000 system as compared to 0.25 mM single TPPB solution (Table 1). This is a relevant proof for synergetic behavior in the mixed system.

Table 1
Self-diffusion coefficients, D_S, hydrodynamic radius, R_H, number of aggregation, N_{agg}, and fraction of the bound substrate, P_b, for the systems based on TPPB and PEG-20,000.

System	$D_{s,sur} \times 10^{10}$ ($m^2\ s^{-1}$)	R_H (nm)	N_{agg}	P_b (%)
0.25 mM TPPB	1.37	2.1	29	
0.25 mM TPPB + 1 mM S3	1.09	2.5	53	3.5
0.25 mM TPPB + 1 mM S3 + 0.05 M PEG-20,000	1.04	2.4	61	15
1 mM TPPB	0.86	3.2	108	
1 mM TPPB + 1 mM S3	0.88	3.1	101	27
4 mM TPPB	0.68	4.1	220	
4 mM TPPB + 1 mM S3	0.74	3.7	170	55

3.2. The zeta potential and counterion binding study

The key factor contributing to the micellar rate effect of cationic surfactants on basic hydrolysis of esters is electrostatic attraction between anionic reagents, i.e., OH ions, and positively charged micellar surface. Therefore, the zeta potential (ξ) values and the degree of counterion binding (β) of TPPB micelles are measured, which may provide evidences of the charge character of aggregates. Data in Fig. 3 and S1–S5 testify that extremely low zeta potential values occur, which may result from (i) the high degree of counterion binding or shielding effect of PEG-20,000 toward the cationic head groups. In single TPPB solution, the ξ value of ca. 60 mV and the β value of 0.8 are found around the cmc [48].

The counterion binding is examined by methods of potentiometry with the bromine selective electrode. Fig. 4 shows potentiometric data for the TPPB–PEG systems. A good linearity is observed for both solutions below the breakpoints, with the Nernst slopes equal to 56 and 58 mV/equiv. As shown, a linear ΔE vs. $\log a_{Br}$ dependence holds good up to the critical points (C_{cr}) for both solutions, while above C_{cr}, plots deviate remarkably from linearity. C_{cr} values determined as break points in the $\Delta E - \lg C$ plots equal 0.5 and 0.8 mM in the case of TPPB–PEG-1000 and TPPB–PEG-20,000 systems, respectively. Meanwhile, tensiometry measurements (data are not shown) revealed two critical points, i.e. critical aggregation concentration (cac) attributed to the formation of the polymer bound micelles, and concentration of the polymer saturation (cps) indicating the appearance of the polymer free micelles. The cacs of 0.09 and 0.05 mM and cpss of 0.9 and 1.0 mM were found for TPPB–PEG-1000 and TPPB–PEG-20,000 systems, respectively. In other words, potentiometric data (Fig. 4) are

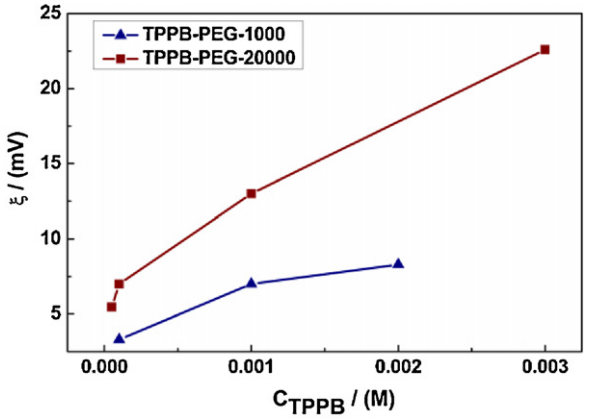

Fig. 3. ξ-potential of TPPB–PEG mixed systems as function of the surfactant concentration (0.05 M PEG); 25 °C.

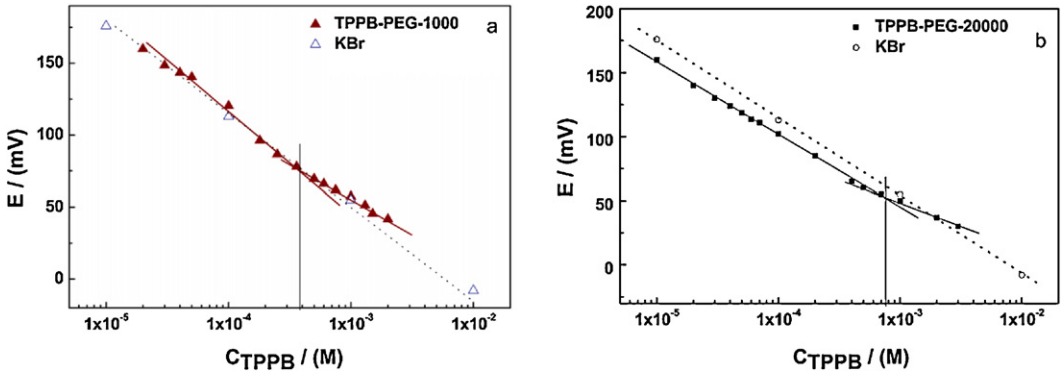

Fig. 4. The potentiometric data for the TPPB-PEG mixed systems (a – PEG-1000, b – PEG-20,000) with using the Br-selective electrode; 25 °C.

insensitive to the cac value. Such behavior can be explained by several ways. First, due to low cac values, changes in the slope in the potentiometry data in this range may be indistinct. Second, premicellar assemblies are probably formed above the tensiometry cac, instead of true micelles, which have low aggregation numbers and highly dissociated head groups. This assumption is in line with the common viewpoint [14–17], emphasizing the formation of small micelles in polymer–surfactant system beyond the cac. Presumably, aggregates formed above the C_{cr} (Fig. 4) are the polymer free micelles. The degree of counterion binding β decreases from ca. 0.6–0.7 (near the cmc) to 0.4 at higher TPPB concentrations (Fig. 5), which is in line with an increase in the zeta potential values (Fig. 3). These β values are much lower as compared to single TPPB solutions (β = 0.8) [48].

Data in Figs. 3–5 can be summarized as follows. First, different types of aggregates may co-exist in mixed solutions, i.e. pre-micellar assemblies with uncompensated but low cooperative surface charge; true micelles formed around C_{cr}, with the moderate β value; and higher charged aggregates prevailing within the concentration range of 0.5 to 3 mM. Second, despite the fact that as a whole, mixed TPPB–PEG aggregates are higher dissociated, their zeta potentials are much lower as compared to single TPPB solution. The conclusion arises that the presence of the polymer is responsible for these differences. Analogous effect has been previously observed in the sodium dodecyl sulfate–PEG system, in which only slight negative potential of −1.4 mV was revealed [64]. Therein, both shielding and probable medium effects were considered, since a high PEG concentration was used. In our case, both effects should also be taken into account, because the location of polymers in vicinity of head groups is established [14–17]. Therefore, the steric hindrance and the polymer induced changes in the micropolarity are probable.

Thus, the factor of electrostatic attraction of anionic reagents to cationic micelles determining the acceleration of ion–molecular reactions is expected to be less favorable in the case of mixed systems as compared to single TPPB micelles.

3.3. Catalytic activity

Within the framework of kinetic study the hydrolysis of phosphonates S1 and S2 of different hydrophobicity is examined. For both TPPB–PEG systems, the higher observed rate constants are found for hydrolyses of the phosphonates as compared to single TPPB solution (Figs. 6 and 7). Effectiveness of catalysts increases in the following order: TPPB < TPPB–PEG-1000 < TPPB–PEG-20,000. A ca. 2-fold and 1.5-fold increase in catalytic activity occurs in these series for hydrolyses of phosphonates S1 and S2 respectively. Single PEG solution has no catalytic effect, and therefore the formation of mixed polymer-colloid catalysts instead of single TPPB micelles is responsible for the increase in the micellar rate effect. Moreover, a marked shift to the lower concentrations occurs for the k_{obs} vs. C dependences in the presence of PEGs (Figs. 6 and 7), which indicates a decrease in cacs of mixed systems as compared to single TPPB solution. These findings can be considered as reliable arguments for the synergetic behavior in the binary TPPB–PEG systems. Kinetic data treated in terms of Eqs. (3) and (4) (Table 2) make it possible to highlight the factors contributing to the enhancement of catalytic effects with the addition of PEGs. For the less hydrophobic phosphonate S1, a marked difference in the reactivity occurs

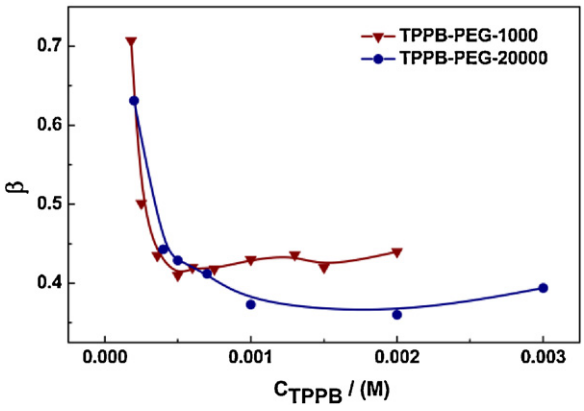

Fig. 5. The degree of counterion binding for TPPB–PEG systems as function of the surfactant concentration; 25 °C.

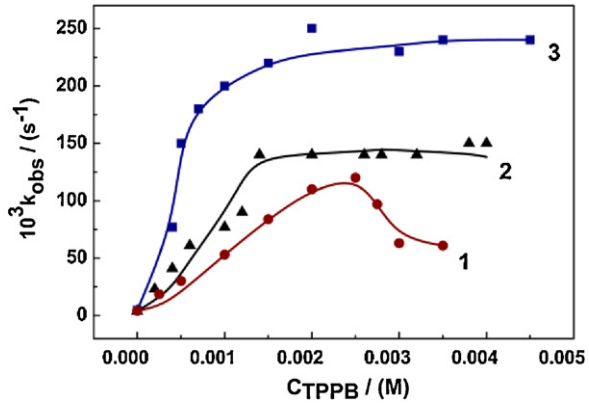

Fig. 6. The dependence of the observed rate constant of the basic hydrolysis of S1 on the surfactant concentration in the single TPPB micelles (1), TPPB–PEG-1000 (2) and TPPB–PEG-20,000 (3) mixed systems; symbols are experimental points, lines are calculated values; 0.001 M NaOH; 0.05 M PEG; 25 °C.

Table 2
The results of the treatment of kinetic data (Figs. 6 and 7) in terms of Eqs. (3) and (4).

	$k_{2,m}$ ($M^{-1}s^{-1}$)	K_S (M^{-1})	K_{OH} (M^{-1})	F_m	F_c	$F_m \times F_c$	k_{max}/k_w
Phosphonate S1							
TPPB	0.37	1630	145	0.093	290	27	30
TPPB–PEG-1000	0.60	926	140	0.16	240	37.6 (38.6)	38
TPPB–PEG-20,000	1.27	2050	82	0.31	190	53.3 (54.6)	54
Phosphonate S2							
TPPB	0.48	3990	281	0.16	585	93	107
TPPB–PEG-1000	0.13	9860	1557	0.043	2658	113	127
TPPB–PEG-20,000	0.17	11275	1047	0.052	2050	106	137

between the single and mixed systems, as well as between the two polymer–colloid systems themselves.

Concentration factor F_c decreases in the TPPB–PEG systems as compared to single TPPB micelles (Table 2, Fig. S6). This effect is due to the reducing of binding constants of substrate (for TPPB–PEG-1000 system) and nucleophile (for TPPB–PEG-20,000 system) (Table 2). At the same time, the binding constant of phosphonate S1 with mixed TPPB–PEG-20,000 aggregates is much higher as compared to both single micelles and those admixed with PEG-1000. The lower K_{OH} values for TPPB–PEG systems are in agreement with predictions based on low values of zeta-potentials of mixed aggregates (Fig. 3). The higher reactivity of TPPB–PEG systems versus single micelles seems to result from a marked increase in the second order rate constant in aggregates (Table 2), i.e., successive a ca. twofold increase in $k_{2,m}$ occurs with the transition from single TPPB micelles to TPPB–PEG-1000 system and further to the TPPB–PEG-20,000 system.

In the case of more hydrophobic substrate S2, the opposite trends are observed. The change in the factor of concentration determines the enhancement in the catalytic activity of the substrate with the PEG addition. A ca. 4.5- and 3.5-fold increase in F_c occurs in the presence of PEG-1000 and PEG 20,000, respectively (Fig. S6), which results from an increase in binding constants of both reagents (Table 2). The increase in the substrate binding constants is in agreement with self-diffusion data, demonstrating the growth of P_{mic} of the model substrate S3 in the presence of PEG-20,000 (Table 1). At the same time, a ca. 5-fold and 3-fold raise of K_{OH} in the presence of PEG-1000 and PEG-20,000, respectively contradict the low zeta-potentials (Fig. 3). This disagreement may originate from the drastic influence of organic species on the micellization of surfactants, which sharply increases with their hydrophobicity [9]. This is also evident from the impact of the model substrate S3 on the self-diffusion coefficients and aggregation numbers of the TPPB micelles (Table 1), although S3 is much less hydrophobic than S2. Therefore the larger aggregates with more cooperative surface charge can be formed in the presence of S2, which would exhibit higher binding capacity toward OH-ions. Thus, for all the systems studied, the higher binding constants are calculated for the more hydrophobic substrate itself and its nucleophilic partner. The higher concentration factor for the more hydrophobic substrates is a common trend of the micellar catalysis, which is usually accompanied by a decrease in the factor of the microenvironment. Indeed, a roughly threefold reduction of F_m is observed in the presence of PEG (Table 2, Fig. S6), which is a minor trend in this case, yet.

To sum it up, structural and charge characteristics of mixed TPPB–PEG systems are studied, which may influence the catalytic activity of the systems toward basic hydrolyses of phosphonic acid esters. The interdependence of aggregates and substrates are revealed from symbate changes in their self-diffusion coefficients. Unlike single TPPB micelles, much lower zeta-potentials of mixed systems are found, although the counterion binding of aggregates decreases with the addition of PEG. This finding predicts the attenuation of catalytic effect of mixed systems due to the decrease in the electrostatic attraction of OH-ions to the micellar surface. In actual fact, a 1.5–2-fold increase in the reactivity of phosphonates occurs in mixed TPPB–PEG systems. This effect along with the polymer induced shift of the onset of the rate acceleration toward the lower concentrations provides strong evidences for synergetic aggregation behavior in the TPPB–PEG systems. The quantitative treatment of kinetic data makes it possible to shed light on the factors of catalytic action. In the case of the hydrolysis of S1, the increase of microenvironmental factor, F_c is responsible for the higher catalytic effect of mixed systems as compared to single TPPB micelles, while the factor of concentration decreases. The opposite trend is observed for the hydrolysis of hydrophobic phosphonate S2, for which an increase in the micellar rate effect with the PEG addition is mainly contributed by the growth of the factor of concentration.

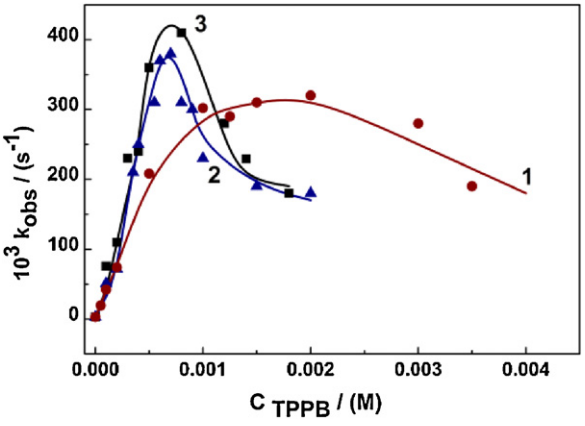

Fig. 7. The dependence of the observed rate constant of the basic hydrolysis of S2 on the surfactant concentration in the single TPPB micelles (1), TPPB–PEG-1000 (2) and TPPB–PEG-20,000 (3) mixed systems; symbols are experimental points, lines are calculated values; 0.001 M NaOH; 0.05 M PEG; 25 °C.

Acknowledgement

This work is supported by the State contract No. 2012-1.2.1-12-000-1004-027.

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.2012.11.071.

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