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# Supramolecular catalytic systems based on bolaform pyrimidinic surfactants: the counterion effect

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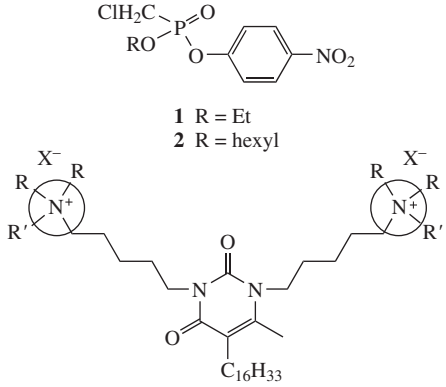
**The catalytic effect of new amphiphilic pyrimidinic compounds with two ammonium head groups and different kinds of counterions, inorganic bromide anions and hydrophobic tosylate anions, was studied and compared with that of conventional cetyltrimethylammonium surfactants with bromide and tosylate counterions.**

Self-assembling systems based on amphiphilic compounds are of interest from both fundamental and practical viewpoints. They are typical biomimetic systems capable of interacting *via* the guest–host mechanism.[1–3] The compartmentalization of guest molecules within nanosized aggregates results in a sharp increase in their local concentrations (the concentration factor) and changes of their microenvironment (the microenvironment factor), which then affect their thermodynamic stability and corresponding quantitative characteristics. From the practical viewpoint the capacity of amphiphiles to aggregate and solubilize guest molecules can be used for designing nanocontainers, nanoreactors, *etc*.[4–9] Our sphere is the formation of nanoreactors for the hydrolysis of phosphorus acid esters by noncovalent strategy in single amphiphile solutions and mixed amphiphile–polymer systems.[10–12] The transfer of a phosphoryl group is one of the most fundamental chemical and biochemical reactions. Besides, the motivation of such investigations is the search of effective catalytic compositions for the destruction of phosphorus acid esters related to ecological toxicants.[13–15] A direction developed in our recent works concerns the design of catalytic systems based on amphiphilic pyrimidinic (AP) compounds, in particular, uracil derivatives. The self-assembly of the macrocyclic pyrimidinic surfactants with two 5(6)-alkyl-substituted uracil moieties bridged together by polymethylene chains and their acyclic analogues with two hydrophilic groups related to gemini or bolaform amphiphiles were studied.[16,17] In this work, new AP compounds with bromide (APB) and tosylate (APT) counterions are synthesized and their catalytic effect towards hydrolysis of *O*-*p*-nitrophenyl-*O*-alkylchloromethylphosphonates [alkyl = ethyl (**1**), hexyl (**2**)] is studied (Scheme 1). The initial motivation of such investigations is the development of effective nanoreactors for important chemical reactions. However, as the information on the catalytic properties of amphiphilic systems becomes accumulated and systematized it provides insight into the aggregative behaviour of new amphiphilic compounds through the examination of their catalytic behaviour. In particular, certain regularities are revealed for the hydrolysis of phosphorus acid esters in direct micellar solutions.[18–20] One of the well established empirical findings is that the sign of the catalytic effect (catalysis/inhibition) on ion-molecular reactions is determined by the charge of aggregates. Cationic micelles accelerate basic hydrolysis by concentrating the reagents in micelles. Organic substrates are effectively solubilized in the nonpolar micellar interior, while hydroxide ions are attracted to the positively charged micellar surface due to electrostatic forces. On the contrary, the inhibition of hydrolysis in anionic micelles is due to the electrostatic repulsion of OH ions from the similarly charged head groups, resulting in the separation of reagents. Knowledge of this and others tendencies makes it possible to analyze the reasons of deviations from them, including those related to the structural factor (*i.e.*, changes in sizes and shapes of aggregates, in the surface potential, the counterion binding, *etc.*).




**Scheme 1** The chemical structures of substrates and bolas.

In this work, the kinetics of basic hydrolysis of phosphonates **1** and **2** in aqueous solutions of APB and APT is measured by spectrophotometry (Figures 1, 2). The aggregation behaviour of the APB and APT systems is covered elsewhere.[21] The mechanism of basic hydrolysis of organophosphorus compounds is well established.[15] Hydrolysis of *p*-nitrophenyl esters of phosporus acids proceeds through P–OAr bond fission with quantitative liberation of the *p*-nitrophenoxide ion. These substrates are widely explored in aqueous solutions and organized systems of different morphologies.[2,3,15] Therefore, they are very suitable for comparing the catalytic activities of different systems. To test whether new dimeric AP surfactants obey the typical behaviour, their catalytic effect is compared with the influence of conventional cetyltrimethylammonium (CTA) surfactants with bromide

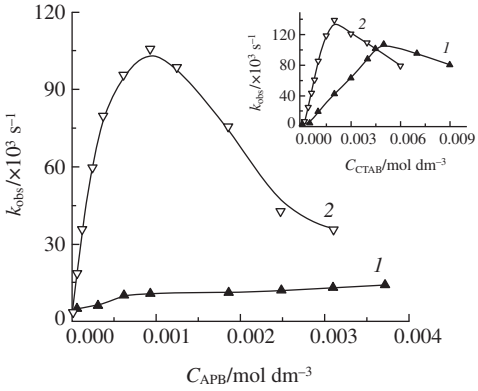



**Figure 1** Observed rate constants of hydrolyses of (*1*) **1** and (*2*) **2** as functions of the APB concentration; 0.001 M NaOH; 25 °C. Inset: observed rate constants of hydrolyses of (*1*) **1** and (*2*) **2** as functions of the CTAB concentration; 0.001 M NaOH; 25 °C.

(CTAB) and tosylate (CTAT) counterions. Substantial differences are observed between the reactivities of phosphonates **1** and **2** in the single-head cationic surfactants. Hydrolysis of more hydrophobic substrate **2** is accelerated by 47 and 35 times in the CTAB and CTAT micelles, respectively (Figures 1, 2). Less hydrophobic phosphonate **1** hydrolyzes in different ways in the micellar solutions of these surfactants. A 25-fold increase in $k_{obs}$ occurs in the CTAB micelles, while almost no effect is observed in the CTAT solution. A slight minimum in the $k_{obs}$ *vs.* [surfactant] plot near the critical micelle concentration (cmc) is probably caused by the primary salt effect in the presence of monomer surfactant. A rate enhancement for the reaction of anionic nucleophiles is typical of cationic micelles. The higher acceleration found for the more hydrophobic substrate **2** is due to its higher affinity towards the nonpolar micellar microenvironment resulting in stronger binding with micelles as compared to substrate **1**. The higher catalytic effect of CTAB as compared to CTAT is probably due to the higher surface potential of the CTAB micelles, which provides the effective electrostatic attraction between OH ions and the micelles. This assumption is in line with the lower degree of the counterion binding for bromide counterions in comparison with organic ions.[21–24]

The acceleration of hydrolyses of **1** and **2** in the presence of APB occurs, which correlates with the cationic character of the APB head groups (Figure 1). The observed rate constants of hydrolysis of **2** in the APB and CTAB solutions are commensurable (maximum values differ by 1.3 times), with the maximum in the $k_{obs}$–$C_{APB}$ dependence shifted to the lower concentrations, as compared to CTAB solution. This is due to the lower

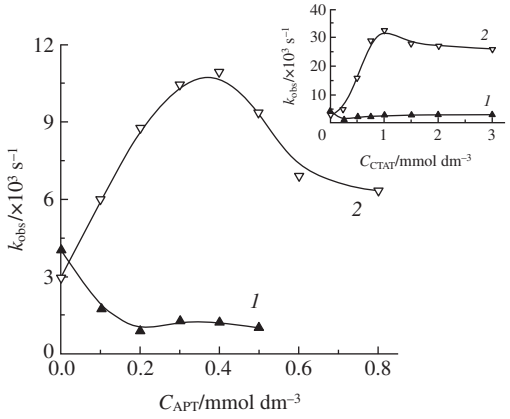



**Figure 2** Observed rate constants of hydrolyses of (*1*) **1** and (*2*) **2** as functions of the APT concentration; 0.001 M NaOH; 25 °C. Inset: observed rate constants of hydrolyses of (*1*) **1** and (*2*) **2** as functions of the CTAT concentration; 0.001 M NaOH; 25 °C.

cmc value of APB (0.4 mM) compared to CTAB (0.85 mM) as evident from the surface tension data.[21] These systems demonstrate a quite different catalytic effect on the hydrolysis of **1**, namely, about 25-fold and 3-fold accelerations occur for CTAB and APB, respectively. If the micellar systems are considered as nanoreactors for the destruction of toxic organophosphorus compounds, the following conclusions can be made: (i) the efficiency of APB is a little less than that of CTAB; (ii) at the same time, APB needs the lower concentrations to reach the maximum catalytic activity as compared to CTAB; (iii) bola APB demonstrates marked substrate specificity; the $k_{obs}$ values for **1** and **2** differ almost tenfold near the cmc in the APB solution against 1.2-fold in the CTAB solution.

Kinetic data for the APT system are given in Figure 2. The micellar rate effect is observed at the concentrations lower than the tensiometric cmc 0.00013 M,[21] which is probably due to the pre-micellar aggregation and/or the promotion of micellization by substrates. The $k_{obs}$ *vs.* $C_{APT}$ dependences for the hydrolyses of **1** and **2** in the APT micellar system differ markedly from those of conventional surfactants CTAB and CTAT and from those of the dimeric surfactant APB. An inversion in the catalytic effect (catalysis/inhibition) is observed depending on the substrate hydrophobicity. A low four-fold acceleration of hydrolysis of **2** and nontypical inhibition of basic hydrolysis of **1** for cationic micelles should be noted. The reasons of such deviation from the typical behavior for cationic surfactants are revealed when the pH *vs.* $C_{APT}$ dependence for APT solutions is examined. Unlike the three other surfactants studied, a sharp decrease in pH occurs in the APT system on reaching the cmc (Figure 3), which is confirmed by both, the pH-meter measurements and the indicator probes. In the APB solution like in the systems based on the conventional CTA surfactants the pH remains near the neutral value throughout the whole concentration range measured. A probable reason for this was assumed to be the geometry of the AP compounds (Scheme 1), in particular, a steric hindrance around the head groups preventing the counterion binding. As distinct from CTAB and CTAT, the head groups of bolas APB and APT bear ethyl groups instead of smaller methyl ones. Besides, the presence of two heads linked by flexible spacer allowed their approaches to be an additional source for the steric barrier especially for the bulky *p*-toluene sulfonate anions. On the other hand, a rigid uracil fragment in the spacer prevents the too close approach of heads. This favours the dissociation of the head groups, which is supported by the NMR self-diffusion data.[21] Therefore, the strong polarization up to the ionization of water molecules in solvate shells of head groups can occur due to cooperative interactions of the dipoles of water with a high uncompensated micellar charge. Thus, hydroxide ions and conjugated hydroxonium ions are generated (Scheme 2). Unlike bulky organic ions, smaller hydroxide ions can bind with head groups, while residuary free protons acidify the system. Thus, the inhibition of hydrolysis of **1** and low acceleration of hydrolysis of **2** are due to the decrease in pH with surfactant concentration. We tested if other inorganic ions (*e.g.*, bromide

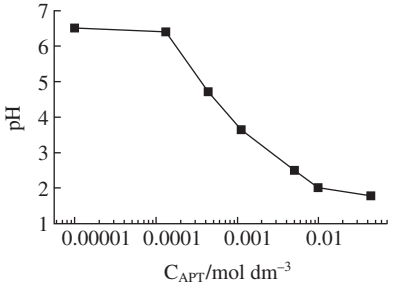
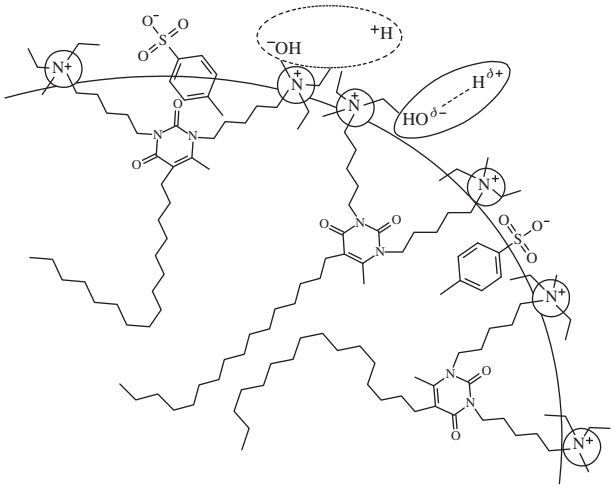



**Figure 3** The dependence of solution pH on the surfactant concentration.



**Scheme 2** Schematic representation of the structure of an APT micelle.

ions) are capable of compensating the abundant micellar charge of APT similar to OH ions. Initially, the addition of sodium bromide retarded the decrease in solution pH with the APT concentration. Nevertheless, a further increase in the surfactant concentration followed the acidification of the system. Probably, only such small hydrophilic ions as $OH^-$ can easily overcome the APT head steric barrier. Incidentally, a similar effect was observed in the polyethyleneimine aqueous solutions in the presence of the multicharged lanthanum ions.[11] The formation of the lanthanum hydroxo complexes was also followed by the deprotonation of water molecules and acidifying the system by two units of pH. When hydrolysis was carried out at higher pH or at a fixed [APT]/[OH] ratio, an effective catalysis occurred in the case of both phosphonates (Figure 4). An almost two orders of magnitude increase in $k_{obs}$ is observed.

In conclusion, the catalytic effect of new dimeric pyrimidinic surfactants towards basic hydrolysis of *O*-*p*-nitrophenyl-*O*-alkylchloromethylphosphonates [alkyl = ethyl (**1**) or hexyl (**2**)] is examined and compared with the rate effect of conventional surfactants CTAB and CTAT with similar counterions. Both CTAB and APB solutions accelerate hydrolyses of phosphonates

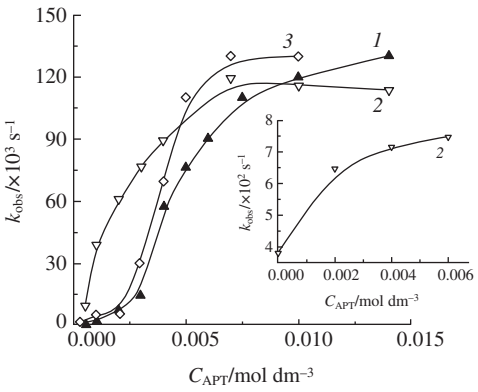



**Figure 4** Observed rate constants of hydrolyses of (*1*, *3*) **1** and (*2*) **2** as functions of the APT concentration; (*1*, *2*) [APT]:[NaOH] = 1:2; (*3*) 1:3; 25 °C. Inset: observed rate constant of hydrolysis of **1** as function of the APT concentration; [NaOH] = 0.01 mol dm$^{-3}$; 25 °C.

**1** and **2**. Surfactants with hydrophobic anions demonstrate a different behaviour, namely, hydrolysis of phosphonate **2** is accelerated by CTAT and APT micelles, while that of less hydrophobic substrate **1** is retarded by the APT micelles unless an alkali excess is used. This deviation from the typical behaviour of cationic surfactants is due to the decrease in the solution pH with the APT concentration above the cmc.

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