Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2008, **18**, 158–160

Mendeleev Communications

Supramolecular catalytic systems based on dimeric pyrimidinic surfactants and polyethyleneimine

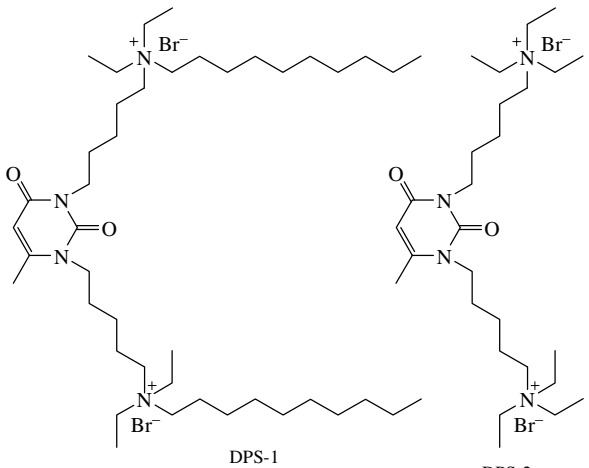
Lucia Ya. Zakharova,*[a] Vyacheslav E. Semenov,[a] Mikhail A. Voronin,[b] Farida G. Valeeva,[a] Lyudmila A. Kudryavtseva,[a] Rashit Kh. Giniatullin,[a] Vladimir S. Reznik[a] and Alexander I. Konovalov[a]

[a] *A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, 420088 Kazan, Russian Federation. Fax: +7 8432 73 2253; e-mail: lucia@iopc.knc.ru*
[b] *Kazan State Technological University, 420015 Kazan, Russian Federation*

DOI: 10.1016/j.mencom.2008.05.016

Cationic dimeric pyrimidinic surfactants have been synthesised; the aggregation and catalytic properties of supramolecular systems based on these surfactants and polyethyleneimine have been studied.

Supramolecular systems based on surfactants and polymers are of interest in colloid and polymer chemistry, catalysis, ecology, biology, *etc*.[1–3] Data on self-organization in aqueous polyethyleneimine (PEI) solutions and their complexes with surfactants are available.[4–6] The catalytic activity of the PEI–water system has been studied.[7–9] In contrast, information on the catalytic properties of polymer–surfactant complexes including those based on PEI is scarce.[10–13] Supramolecular catalysts based on dimeric pyrimidinic surfactants and their complexes with polymers have not been explored previously. In this work, we synthesised two dimeric pyrimidinic surfactants (DPSs): a structural analogue of geminis, 1,3-bis[5-(*n*-decyldiethylammonium)pentyl]-6-methyluracil dibromide (DPS-1), and a typical bolaform surfactant, 1,3-bis[5-(triethylammonium)pentyl]-6-methyluracil dibromide (DPS-2) (Scheme 1). Dimeric surfactants can be classified as bolaform or gemini surfactants. Bolaamphiphiles (bolaform surfactants or bolas) are molecules that have hydrophilic groups at both ends of a hydrophobic chain.[14,15] Gemini surfactants consist of two hydrophobic chains and two hydrophilic head groups linked by a spacer.[16,17] Due to their structural features, bolas and geminis demonstrate a marked ability for self-organization at the interface or in bulk solutions. Previously,[10–13] we used multicomponent self-assembling systems for the design of nanoreactors. Nanosized reactors based on macrocyclic pyrimidinic surfactants and their complexes with PEI were designed.[13] This work extends the approach to the study of the catalytic effect of aqueous solutions of the acyclic analogues DPS-1 and DPS-2 and their mixtures with PEI toward the hydrolysis of *O*-alkyl-*O*-*p*-nitrophenylchloromethylphosphonates (Scheme 1). Since the catalytic activity of the supramolecular systems is largely due to their aggregative ability, the colloid properties of the above systems were also investigated.



1 R = Et
2 R = *n*-hexyl

The transfer of a phosphoryl group is a fundamental chemical and biochemical reaction.[18] Phosphorus acid esters are widely used as pesticides, drugs and nerve gases.[19] The hydrolysis of phosphorus acid esters has been studied in detail in aqueous alkali solutions,[20] in single surfactant[21–24] and PEI[7–9] solutions. Amines (including polyamines) accelerate the hydrolysis of phosphorus acid esters *via* general basic catalysis.[7]

DPS-1 was synthesised by the quaternization of aliphatic nitrogens in 1,3-bis(5-ethylaminopent-1-yl)-6-methyluracil with *n*-bromodecane.[25] DPS-2 was prepared by the reaction of 1,3-bis-(5-bromopent-1-yl)-6-methyluracil with triethylamine in MeCN.[†] Substrates **1** and **2** were prepared according to a published procedure.[26] PEI with an average molecular mass of 50000–60000 (50% aqueous solution) (polyethyleneimine chains are branched, with primary, secondary, and tertiary nitrogens in a ratio of 1:2:1) from Aldrich was used. The molar concentrations of PEI solutions are given on a monomer basis. Aggregation was studied by tensiometry using the du Nouy ring detachment method. The experiments were described in details elsewhere.[27] The kinetics of hydrolysis was monitored by spectrophotometry.[10–13] The reaction mechanism was studied by ^{31}P NMR spectroscopy, which revealed the only phosphorus product with chemical shift δ 14.5 ppm corresponding to *O*-ethylchloromethylphosphonic acid.

Figure 1 shows surface tension isotherms for single surfactant solutions and binary surfactant–PEI systems. Pronounced break

[†] *Synthesis of DPS-2.* 1,3-Bis(5-bromopent-1-yl)-6-methyluracil (2.1 mmol) and a six-fold excess of NEt_3 in MeCN (50 ml) were refluxed for 20 h. The solvent was distilled off. The residue was thoroughly triturated in diethyl ether (5×30 ml), each time decantated and finally the solvent was evaporated. Yield, 80%. Hygroscopic solid, mp 75 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.56 [s, 1H, $C(5)_{ur}H$], 3.95–3.89 [m, 4H, $2N(3)_{ur}CH_2$, $2N(1)_{ur}CH_2$], 3.48–3.35 (m, 16H, $8NCH_2$), 2.26 [s, 3H, $C(6)_{ur}Me$], 1.92–1.60 (m, 12H, $6CH_2$), 1.40 (m, 18H, $6NCH_2$*Me*). Found (%): C, 51.62; H, 8.86; Br, 25.64; N, 9.02. Calc. for $C_{27}H_{54}Br_2N_4O_2$ (%): C, 51.76; H, 8.69; Br, 25.51; N, 8.94.

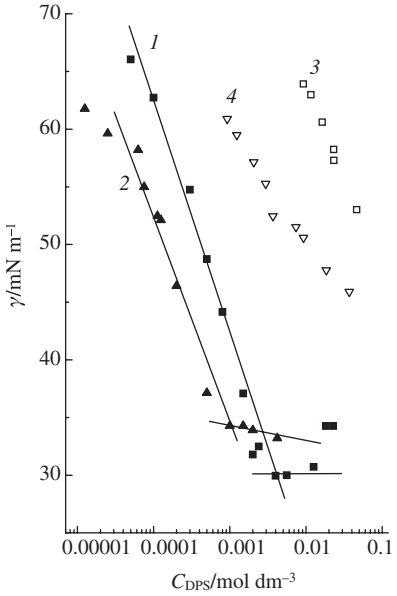


Figure 1 Surface tension isotherms of single (*1*) DPS-1 and (*3*) DPS-2 systems and binary (*2*) DPS-1/PEI and (*4*) DPS-2/PEI systems (0.05 M PEI); 25 °C.

points in the γ–lg *C* plots indicate aggregation in both single [critical micelle concentration (CMC) of 0.003 mol dm^{-3}] and binary DPS-1/PEI [critical aggregation concentration (CAC) 0.0006 mol dm^{-3}] systems. A marked decrease in the CMC in the presence of the polymer indicates a high mutual affinity between the components and provides evidence for the formation of mixed DPS-1/PEI assemblies. Such a behaviour is not typical of cationic surfactant and neutral polymer or weak polyelectrolyte pairs like an unbuffered PEI solution. As distinct from anionic surfactants, cationic surfactant/polymer systems demonstrate a lower mutual affinity between the components. In DPS-2 solutions, the critical points are not found in the γ–lg *C* plots within the concentration range studied (Figure 1). At the same time, a considerable decrease in the surface tension is observed with increasing DPS-2 concentration. Therefore, aggregation occurs under a higher concentration, which is inaccessible by experimental reasons. This can be elucidated by a study of the catalytic effect of DPS-2-based systems. To conclude, the comparison of the surface tension isotherms of DPS-1 and DPS-2 reveals the higher aggregative ability of the more hydrophobic DPS-1 surfactant as compared to DPS-2.

Figure 2(*a*) shows kinetic data for the basic hydrolysis of phosphonates **1** and **2** in the single DPS-1 system. For phosphonate **1**, a fourfold decrease in the apparent rate constant occurs below the CMC as compared to the reaction in water. Above the CMC, the rate constant increases up to its value in an aqueous alkali solution. In the case of phosphonate **2**, k_{obs} changes only slightly below the CMC, while above the CMC a fourfold rate acceleration occurs, as compared to an aqueous alkali solution. Critical points in the kinetic curves (Figure 2) are in a good agreement with the results of tensiometry (Figure 1). In the binary DPS-1/PEI solution, an acceleration of the hydrolysis of both phosphonates occurs [Figure 2(*b*)]. For more hydrophobic phosphonate **2**, the catalytic effect reaches one order of magnitude as compared to the single PEI solution. The higher catalytic effect for the more hydrophobic substrate probably indicates a considerable contribution of solubilization to reagent binding in both the absence and the presence of the polymer. The regularities found (the acceleration of phosphonate hydrolysis and substrate specificity) are typical of the micellar solutions of cationic surfactants.[21–24]

In Figure 3, the kinetic data for the hydrolysis of phosphonates **1** and **2** in the DPS-2-based systems are shown. The rate

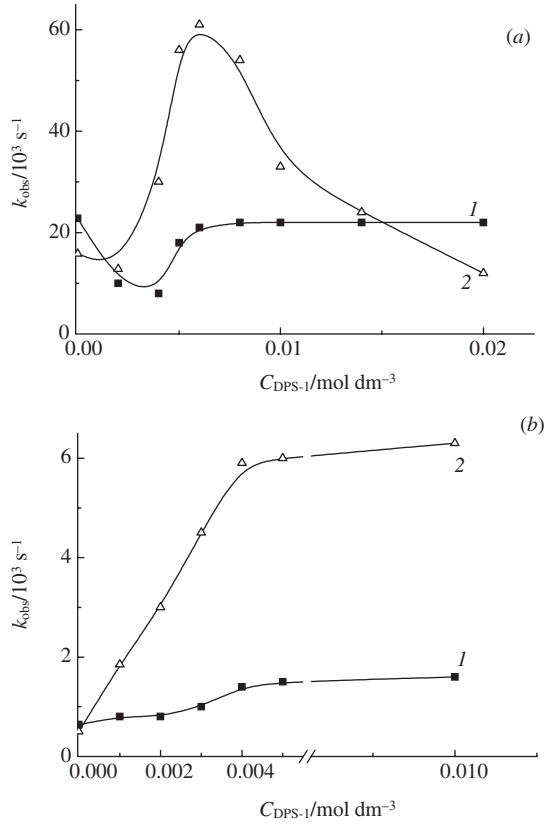


Figure 2 Observed rate constants of the hydrolysis of (*1*) **1** and (2) **2** as functions of DPS-1 concentration in (*a*) the single DPS-1 system (0.005 M NaOH) and (*b*) the DPS-1/PEI system (0.05 M PEI, pH 10.5); 25 °C.

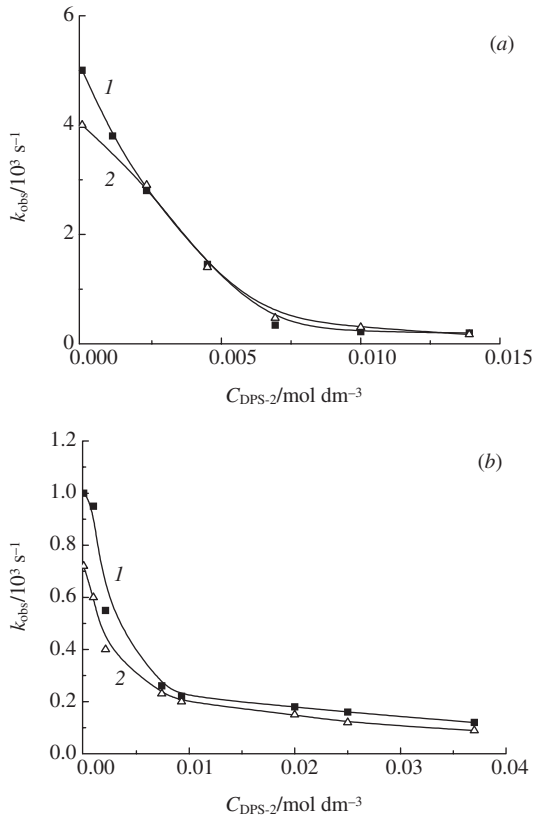


Figure 3 Observed rate constants of the hydrolysis of (*1*) **1** and (2) **2** as functions of DPS-2 concentration in (*a*) the single DPS-2 system (0.001 M NaOH) and (*b*) the DPS-2/PEI system (0.05 M PEI, pH 10.5); 25 °C.

Table 1 Quantitative treatment of kinetic data in terms of equation (1).

System	Substrate	$k_{cat}/10^3$ s^{-1} [a]	K_S/dm^3 mol^{-1}	K_{cat}/k_0
DPS-1	**1**	61	174	3.9
DPS-1/PEI	**1**	1.5	66	2.3
DPS-1/PEI	**2**	6.0	138	12
DPS-2	**1**	0.2	286	0.04
DPS-2	**2**	0.17	472	0.04
DPS-2/PEI	**1**	0.1	930	0.12
DPS-2/PEI	**2**	0.1	713	0.12

[a]Plateau value.

effect of this surfactant on the phosphonate hydrolysis dramatically differs from that of DPS-1 (Figure 2). An 8–25-fold inhibition of the reaction is observed in both the single DPS-2 solution and the binary DPS-2/PEI system. The kinetic data (Figure 3) provide indirect evidence for aggregation in the DPS-2-based systems. Note that the inhibition effect of the cationic surfactant towards the hydrolysis of phosphonates is unexpected.[21–24]

The kinetics (Figures 2 and 3) obeys the formalism similar to the Michaelis–Menten equation for enzyme catalysis:[21]

$$k_{obs} = \frac{k_0 + k_{cat}K_S C}{1 + K_S C}, \quad (1)$$

where K_S is the binding constant of substrate (S), k_0 and k_{cat} (s^{-1}) are the pseudo-first-order rate constants in water and catalytic complexes, respectively, C is the concentration of the micellised surfactant. The results are summarised in Table 1. The high values of binding constants indicate the practically complete transfer of the reaction from water to the aggregates. Note that the binding constants are higher in the DPS-2-based systems. The experimental data are in agreement with the above assumption on the solubilization mechanism of the reagent binding. The inhibition of the reaction in the DPS-2-based solutions is probably due to the localization of the reagents in different phases: a substrate is transferred to the aggregates, while the nucleophile remains in water.

This work was supported by the Russian Foundation for Basic Research (grant no. 07-03-00392-a).

References

1 J. C. Brackman and J. B. F. N. Engberts, *Chem. Soc. Rev.*, 1993, **22**, 85.
2 E. D. Goddard, *J. Colloid Interface Sci*., 2002, **256**, 228.
3 V. A. Sethuraman, K. Na and Y. H. Bae, *Biomacromolecules*, 2006, **7**, 64.
4 S. M. Bystryak and M. A. Winnik, *Langmuir*, 1999, **15**, 3748.
5 B. M. D. O'Driscoll, E. Milsom, C. Fernandez-Martin, L. White, S. J. Roser and K. J. Edler, *Macromolecules*, 2005, **38**, 8785.
6 J. Penfold, I. Tucker, R. K. Thomas, D. J. F. Taylor, J. Zhang and C. Bell, *Langmuir*, 2006, **22**, 8840.
7 R. F. Bakeeva, L. A. Kudryavtseva, V. E. Belskii and B. E. Ivanov, *Zh. Obshch. Khim.*, 1983, **53**, 1058 (in Russian).
8 F. Hollfelder, A. J. Kirby and D. S. Tawfik, *J. Am. Chem. Soc*., 1997, **119**, 9578.
9 F. Avenier, J. B. Domingos, L. D. Van Vliet and F. Hollfelder, *J. Am. Chem. Soc*., 2007, **129**, 7611.
10 L. Yu. Zakharova, F. G. Valeeva, D. B. Kudryavtsev, A. R. Ibragimova, L. A. Kudryavtseva, A. P. Timosheva and V. E. Kataev, *Kinet. Katal*., 2003, **44**, 559 [*Kinet. Catal*. (*Engl. Transl.*), 2003, **44**, 547].
11 L. Ya. Zakharova, A. R. Ibragimova, F. G. Valeeva, A. V. Zakharov, A. R. Mustafina, L. A. Kudryavtseva, H. E. Harlampidi and A. I. Konovalov, *Langmuir*, 2007, **23**, 3214.
12 L. Ya. Zakharova, A. R. Ibragimova, F. G. Valeeva, L. A. Kudryavtseva, A. I. Konovalov, A. V. Zakharov, N. M. Selivanova, V. V. Osipova, M. V. Strelkov and Yu. G. Galyametdinov, *J. Phys. Chem. C*, 2007, **111**, 13839.
13 L. Ya. Zakharova, V. E. Semenov, M. A. Voronin, F. G. Valeeva, A. R. Ibragimova, R. Kh. Giniatullin, A. V. Chernova, S. V. Kharlamov, L. A. Kudryavtseva, Sh. K. Latypov, V. S. Reznik and A. I. Konovalov, *J. Phys. Chem. B*, 2007, **111**, 14152.
14 R. Nagarajan, *Chem. Eng. Commun*., 1987, **55**, 251.
15 J.-H. Fuhrhop and T. Wang, *Chem. Rev.*, 2004, **104**, 2901.
16 F. M. Menger and C. A. Littau, *J. Am. Chem. Soc*., 1993, **115**, 10083.
17 R. Zana, *Curr. Opin. Colloid Interface Sci*., 1996, **1**, 566.
18 F. H. Westheimer, *Science*, 1987, **235**, 1173.
19 Y. C. Yang, J. A. Baker and J. R. Ward, *J. Chem. Rev*., 1992, **92**, 1729.
20 V. E. Bel'skii, *Usp. Khim*., 1977, **46**, 1578 (*Russ. Chem. Rev*., 1977, **46**, 828).
21 I. V. Berezin, K. Martinek and A. K. Yatsimirski, *Usp. Khim*., 1973, **42**, 1729 (*Russ. Chem. Rev*., 1973, **42**, 787).
22 E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem*., 1970, **8**, 271.
23 C. A. Bunton and G. Savelli, *Adv. Phys. Chem*., 1986, **22**, 213.
24 L. S. Romsted, in *Micellization, Solubilization, and Microemulsions*, ed. K. L. Mittal, Press, New York–London, 1977, vol. 2, p. 509.
25 V. E. Semenov, A. D. Voloshina, E. M. Toroptzova, N. V. Kulik, V. V. Zobov, R. Kh. Giniyatullin, A. S. Mikhailov, A. E. Nikolaev, V. D. Akamsin and V. S. Reznik, *Eur. J. Med. Chem*., 2006, **41**, 1093.
26 D. F. Toy and K. H. Rattenbury, *U.S. Patent*, 2922810, 1960.
27 L. Ya. Zakharova, F. G. Valeeva, A. V. Zakharov, A. R. Ibragimova, L. A. Kudryavtseva and H. E. Harlampidi, *J. Colloid Interface Sci*., 2003, **263**, 597.

Received: 12th October 2007; Com. 07/3027