Dedicated to V. F. Mironov on His 60th Anniversary

New Amphiphilic Multiheterocycle: Micelle-Forming Properties and Effect on the Reactivity of Phosphorus Acid Esters

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Abstract—Supramolecular systems based on a novel tetracationic amphiphilic multiheterocycle have been studied by tensiometry, conductometry, pH-metry, spectrophotometry, and dynamic and electrophoretic light scattering. The critical micelle concentration of the system has been determined (0.4 mM), and the possibility of open and closed association models realization has been demonstrated. A high solubilizing ability of the aggregates toward hydrophobic guest species has been revealed. Micellar catalysts based on the new multiheterocycle have shown substrate specificity in the hydrolysis of phosphonates possessing different hydrophobicities.

Keywords: supramolecular systems, multiheterocycle, amphiphile, self-organization, solubilization, substrate specificity

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Broad utility of surfactants in modern technologies and industrial processes stimulates the development of fundamental studies on compositions based thereon. At present, research work in the field of surfactants progresses in accordance with the environmental (socalled "green chemistry" principles) and economic requirements (cost reduction) [1]. As a result, the use of previously traditional surfactants is gradually restricted, and design of novel amphiphilic compounds conforming to the above criteria is stimulated. New amphiphilic building blocks are generally constructed following several approaches:

(1) Replacement of *n*-alkyl substituent in a surfactant molecule by fused aromatic fragments, which makes it possible to obtain chiral supramolecular structures [2] that are important for technologies and biotechnologies;

(2) Transition from monocationic surfactants to socalled gemini surfactants containing more than one head groups and hydrophobic tails, which are characterized by considerably lower critical micelle concentrations [3, 4]; such surfactants turned out to efficiently catalyze oxidation of D-glucose [5], model biochemical condensation reactions with amino acids [6], and reactions involving P–O bond cleavage [7];

(3) Design of so-called supramolecular amphiphiles formed via various non-covalent interactions, which could provide the basis for the creation of new generation materials [8–12];

(4) Covalent attachment of various natural fragments to an amphiphilic compound with the goal of endowing the system with biomimetic properties. The most popular versions of the design of novel amphiphilic building blocks in terms of this approach include introduction of such fragments as mono- [13] and oligo(amino acid) moieties [14], monosaccharide residues [15], oligonucleotide chains [16], and pyridinium or imidazolium heterocycles [17] into surfactant molecules. This makes it possible to reduce the toxicity of the resulting compositions, which is important for biomedicine and obtain efficient catalysts ensuring decomposition of various phosphoruscontaining pollutants.

The above stated determines the importance of the present study which combines approaches to the



Fig. 1. Surface tension isotherm of aqueous solutions of 1 at 25° C.

design of new gemini surfactants and amphiphiles containing a natural fragment and is concerned with physicochemical properties (aggregation ability, catalytic effect) of a novel tetracationic amphiphile containing pyrimidine and 1,2,3-triazole heterocycles, 1,3-bis(6- $\{4-[(1,3-bis\{5-[decyl(diethyl)ammonio]pentyl\}-6$ methyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)methyl]-1H-1,2,3-triazol-1-yl}hexyl)-5-methylpyrimidine-2,4(1H,3H)-dione tetrabromide (1), in aqueous solution (Scheme 1).

The design of such amphiphilic building block was motivated by our earlier experience [18–23] and was dictated by the possibility of involving both



Fig. 2. Concentration dependence of the specific conductivity of aqueous solutions of 1 at 25°C.

hydrophobic interactions with participation of four *n*-decyl groups and intermolecular π -stacking of the extended aromatic system in self-association processes.

Amphiphilic uracil derivative **1** was synthesized by copper-catalyzed Huisgen–Meldal–Sharpless 1,3-dipolar cycloaddition (CuAAC) of diazide **2** with diamine **3** possessing a propargyl group on the pyrimidine ring (Scheme 2). This reaction is known to selectively afford 1,4-disubstituted 1,2,3-triazole derivatives [24–26].

The critical micelle concentration (CMC) of **1** was determined by tensiometry from the inflection point on the surface tension isotherm of its aqueous solution







(Fig. 1). The obtained CMC value (0.4 mM) is lower by almost an order of magnitude than those found for previously studied dicationic surfactants of the same series (CMCs of a large number of pyrimidine-based dimeric surfactants range from 2 to 3 mM) [27-29]. This is likely to be determined by increased hydrophobicity of molecule 1 containing four nonpolar fragments. It should be noted that the CMC of 1 in aqueous solution is almost twice as low as those of previously studied tetracationic surfactants with methylene and hexadiyne spacers [18] (CMC 0.87 and 0.72 mM, respectively). Obviously, the reason is that the aggregation behavior of 1 is largely contributed by the presence in its molecule of three additional heterocyclic fragments which give rise to additional intermolecular π -stacking interactions. Furthermore, the contribution of hydrophobic interactions with

participation of two additional hexamethylene spacers in **1** should also be taken into account.

The CMC value of **1** determined by conductometry (0.2 mM) was twice as low as the tensiometric value, which suggests the formation of premicellar aggregates in solution (Fig. 2). As the concentration of **1** in aqueous solution increased, the pH value insignificantly decreased (Fig. 3). It should be noted that this relationship is typical of most pyrimidine-containing surfactants; however, in some cases, the reduction in pH may achieve 4 units and more [30]. Presumably, in the case of compound **1**, the factor responsible for the reduction of pH (partial ionization of water molecules in the solvation shells of surfactant micelles) is compensated by basic properties of the 1,2,3-triazole fragments in molecule **1**.



Fig. 3. Concentration dependence of pH of aqueous solutions of 1 at 25°C.

An alternative method for the determination of CMC is fluorescent spectroscopy using pyrene as fluorescent probe sensitive to variation of microenvironment. The intensity ratio I_1/I_3 of the first and third vibronic peaks of pyrene at different surfactant concentrations (calculated on the basis of the experimental spectra) is a useful parameter for the estimation of the surfactant aggregation ability in aqueous solution. Figure 4a shows the plot of I_1/I_3 versus surfactant concentration (c_{surf}), which was drawn on the basis of the fluorescence spectra of pyrene in the presence of uracil **1** (Fig. 4b). The inflection point on the I_1/I_3 — c_{surf} plot corresponds to the CMC value (0.37 mM). This value is very similar to that found by tensiometry.

According to the dynamic light scattering data (Fig. 5), two types of aggregates are formed by surfactant **1** in solution: those with a hydrodynamic diameter $D_{\rm H}$ of about 100 nm in the vicinity of CMC and with $D_{\rm H} \leq 2$ nm at a surfactant concentration of 1 mM and higher. Such morphological reorganization via transition from the open association model to closed one is likely to be determined by increasing contribution of hydrophobic effect to the formation of associates, which begins to dominate over stacking interactions as the concentration of **1** rises.

Electrophoretic light scattering study has shown that the ζ potential of aggregates of **1** in the vicinity of CMC is 52.9 mV and that it decreases down to 20 mV



Fig. 4. (a) Plot of the fluorescence intensity ratio of the first and third vibronic peaks of pyrene versus concentration of **1** and (b) emission spectra of pyrene (1) in the absence of surfactant and in the presence of (2) 0.3, (3) 1.0, and (4) 4.4 mM of **1**.

with rise in the surfactant concentration. This fact suggests morphological reorganization of aggregates in the surfactant concentration range from 0.5 to 2.0 mM.

The functional activity of nanosized aggregates formed in aqueous solution was estimated by spectrophotometric study of the solubilizing ability of micellar solutions of 1 toward the hydrophobic azo dye Orange OT. Water-soluble form of the latter show an intensive band in the electronic absorption spectrum in the visible region (λ_{max} 495 nm), which makes it a convenient tool for estimating CMC of surfactants from the electronic absorption spectra of binary system surfactant–dye (Fig. 6b). In this case, the CMC is



Fig. 5. Number averaged size distribution of aggregates of surfactant 1 in aqueous solutions at 25°C; concentration of 1 (1) 0.5, (2) 1.0, (3) 2.2, (4) 4.4, and (5) 10.2 mM.



Fig. 6. (a) Plot of the optical density at λ 495 nm versus surfactant concentration for the binary system 1–Orange OT at 25°C and (b) electronic absorption spectra of the binary system 1–Orange OT at different concentrations of 1; the arrow indicates increase of the concentration of 1 from 0.001 to 4.4 mM; temperature 25°C.

determined as the surfactant concentration at which two linear parts of the corresponding solubilization dependence cross each other (Fig. 6a). Comparing the obtained data with the results of tensiometric study, we can contend that the aggregates formed at a sur-factant concentration of 0.2 mM exhibit low solubilizing ability up to a concentration of 1 mM and that the solubilizing ability sharply increases when the concentration exceeds 1 mM. The solubilizing capacity of aggregates of 1 (S = 0.0129 mol of the dye per mole of the surfactant) is five times higher than that of its monocationic analog (decyltrimethylammonium bromide, S = 0.0027 mol of the dye per mole of the surfactant); i.e., aggregates of 1 are capable of solubilizing a fivefold amount of hydrophobic guest species, which is most likely to result from the larger volume of the hydrophobic domain.

The catalytic activity of aggregates of **1** was evaluated by spectrophotometry using the hydrolysis of alkyl 4-nitrophenyl chloromethylphosphonates (Scheme 3) as model reaction. It was found that addition of amphiphilic multiheterocyclic compound **1** to the reaction mixture inhibits the hydrolysis of phosphonate **5** (alkyl = Et) and significantly accelerates the hydrolysis of **6** (alkyl = *n*-hexyl). These findings may be accounted for by higher hydrophobicity of compound **6** and hence its higher affinity for the nonpolar micelle core as compared to **5**; therefore, phosphonate **6** is more readily concentrated in micelles of **1**. To confirm this assumption, we calculated the substrate–micelle binding



Fig. 7. Plots of the rate constants of alkaline hydrolysis of phosphonates (1) 5 and (2) 6 versus concentration of surfactant 1; 0.001 M NaOH, 25°C.

constants $K_{\rm S}$ and rate constants in the catalytic complex (k_m) for compounds **5** and **6** (see below).

Phosphonate	5	6
K _S	2790	1664
$k_{\rm m} \times 10^3$	0.2	2.0

Analysis of the obtained values shows that our initial assumption implying higher ability of 6 to bind to the nonpolar micelle core is invalid, because $K_{S(5)} >$ $K_{S(6)}$. On the other hand, the rate of hydrolysis of phosphonate 6 in micelles is higher by an order of magnitude than the rate of hydrolysis of 5, which is the obvious factor responsible for the observed catalytic effect. In the case of phosphonate 5, the inhibitory effect may be attributed to the reduction of pH with increase in the concentration of 1 (Fig. 7). As a result, the concentration of hydroxide ions in solution decreases, and the reaction slows down. Thus, the overall catalytic effects of surfactant 1 on the hydrolysis of phosphonates 5 and 6 may be considered as the sum of the above two factors with the difference that reduction of pH predominates for compound 5 while increased reaction rate in the catalytic complex predominates for phosphonate 6.

The obtained data on the aggregation behavior and functional activity (solubilizing and catalytic effects) of amphiphilic multiheterocycle **1** led us to conclude that the described methodology for the design of novel surfactants via a combination of approaches involving

Scheme 3.



the development of new gemini surfactants and amphiphiles containing a natural fragment is practicable, promising, and competitive in the field of creation of polyfunctional materials on the basis of amphiphilic compounds.

EXPERIMENTAL

The ¹H and ¹³C NMR spectra were recorded at 30°C on a Bruker Avance-500 spectrometer (500.13 and 125.77 MHz, respectively) using tetramethylsilane as external standard. The mass spectra (MALDI-TOF) were obtained on a Bruker Ultraflex instrument using 4-nitroaniline as matrix. The IR spectra were recorded from films on a Bruker Vector 22 spectrometer with Fourier transform under standard conditions (spectral range 4000–400 cm⁻¹, resolution 4 cm⁻¹). The elemental compositions were determined using a CHN analyzer EuroEA3028-HT-OM (Eurovector S.p.A.). The electronic absorption spectra were measured with an Analytik Jena Specord PLUS spectrophotometer; the cell path lengths was varied so that the optical density ranged from 0.5 to 0.8.

The surface tension was measured by the Du Noüy ring detachment method using a Krüss K06 tensiometer. The volume of solution for tensiometric measurements was no less than 10 mL. Between measurement, the ring was treated with ethanol and burnt with flame. The specific conductivity was determined with an Inolab Cond 720 conductometer. The pH values of surfactant solutions were measured with a Hanna Instruments HI 9025 pH meter equipped with an HI 1330 glass membrane electrode.

Dynamic and electrophoretic light scattering experiments were carried out with a Malvern Zetasizer Nano instrument equipped with a He–Ne gas laser (4 mW, λ 633 nm). Signals were processed by frequency and phase analysis of scattered light using standard instrument software. In all measurements the scattering angle was 173°. The particle size was calculated by the Stokes–Einstein equation for spherical particles (1).

$$D = \frac{kT}{6\pi\eta R} \,. \tag{1}$$

Here, k is the Boltzmann constant, T is the absolute temperature, η is the solvent viscosity, and R is the hydrodynamic radius. All solutions were filtered through a Millipore filter with a pore diameter of 450 nm to remove dust before measurements.

The fluorecence spectra of pyrene $(1 \times 10^{-6} \text{ M})$ were recorded on a Varian Cary Eclipse G9800A spetrofluorometer at 25°C (λ_{excit} 335 nm). The emission spectra were measured in the range λ 350–500 nm with a scan rate of 120 nm/min using a 1-cm path length cell. The obtained spectra were used to calculate the fluorescence intensities at λ 373 (I_1) and 384 nm (I_3).

The kinetics of the hydrolysis of phosphonates **5** and **6** were studied by spectrophotometry with an Analytik Jena Specord PLUS spectrophotometer by measuring the optical density at λ 400 nm (4-nitrophenoxide ion) under pseudofirst-order conditions. The observed rate constants (k_{obs}) were calculated by Eq. (2).

$$\ln (A_{\infty} - A_{\tau}) = -k_{\rm obs} \,\tau + {\rm const.} \tag{2}$$

Here, A_{∞} and A_{τ} are the optical densities of a solution in the end of the reaction and at time τ , respectively. The calculations were carried out by the weighted least squares method from mean values of three separate measurements differing by no more than 5%.

The kinetic data were quantitatively analyzed using Eq. (3) which implies formation of a substrate-micelle catalytic complex [31].

$$k_{\rm obs} = \frac{k_{\rm w} + k_{\rm cat} K'_{\rm S} c_{\rm I}}{1 + K'_{\rm S} c_{\rm I}}.$$
(3)

Here, k_{obs} is the observed pseudofirst-order rate constant, k_{cat} and k_w are the first-order rate constants in the catalytic complex and in water, respectively, K'_s is the reduced micelle–substrate binding complex, and c_1 is the concentration of amphiphilic multiheterocycle **1**.

Phosphonates **5** and **6** were synthesized according to known method [32].

1,3-Bis(6-azidohexyl)-5-methylpyrimidine-2,4-(1*H*,3*H*)-dione (2). To a solution of 4 g (8.8 mmol) of

1,3-bis(6-bromohexyl)thymine [33] in 100 mL of DMF we added 1.14 g (17.5 mmol) of sodium azide and a catalytic amount of tetrabutylammonium hydrogen sulfate. The mixture was stirred for 10 h at 70°C, the progress of the reaction being monitored by TLC. The mixture was cooled, the solvent was distilled off, 100 mL of chloroform was added to the residue, and the precipitate was filtered off. The filtrate was evaporated to isolate 2.05 g (61%) of diazide 2 as oily material. IR spectrum, v, cm⁻¹: 2096 (N₃), 1700, 1659 (C=O). ¹H NMR spectrum (CDCl₃), δ , ppm (J, Hz): 7.32 s (1H, 6-H), 3.87 t (2H, 3-CH₂, ${}^{3}J_{HH} = 7.3$), 3.72 t $(2H, 1-CH_2, {}^{3}J_{HH} = 7.4), 3.30-3.26 \text{ m} (4H, CH_2N_3),$ 1.87 s (3H, 5-CH₃), 1.67-1.59 m (8H, CH₂), 1.42-1.37 m (8H, CH₂). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 162.0, 151.6, 139.2, 110.9, 49.5, 48.0, 43.7, 44.4, 30.1, 29.7, 29.5, 28.9, 26.4, 12.7. Mass spectrum (MALDI-TOF): m/z 376.4 $[M]^+$ (calculated for C₁₇H₂₈N₈O₂: 376.2). Found, %: C 54.26; H 7.53; N 29.80. C₁₇H₂₈N₈O₂. Calculated, %: C 54.24; H 7.50; N 29.77.

1.3-Bis{6-[4-({1,3-bis[5-(diethylamino)pentyl]-6methyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl methyl)-1H-1,2,3-triazol-1-yl|hexyl}-5-methylpyrimidine-2,4(1H,3H)-dione (4). A solution of 0.85 g (1.9 mmol) of 1,3-bis(5-diethylaminopentyl)-6-methyl-5-(prop-2-yn-1-yl)pyrimidin-2,4(1H,3H)-dione (3) [34] in 30 mL of ethanol was added to a solution of 0.38 g (1.0 mmol) of diazide 2 in 15 mL of ethanol. A solution of 0.08 g (0.40 mmol) of sodium ascorbate and 0.01 g (0.04 mmol) of copper(II) sulfate pentahydrate in 9.5 mL of water was then added, and the mixture was stirred for 16 h at room temperature. The solvent was removed under reduced pressure, the residue was dissolved in chloroform, the solution was treated with charcoal and filtered, and the filtrate was evaporated. Yield 1 g (83%), thick yellow oil. IR spectrum, v, cm⁻¹: 2957, 2935, 2862, 2800, 1696 (C=O), 1642, 1464, 1361, 1247, 1203, 1082, 1047, 801, 769, 731. ¹H NMR spectrum (CDCl₃), δ , ppm: 7.42 s and 7.41 s (2H, 4'-H), 6.93 s (1H, 6-H), 4.28-4.23 m (4H, 1'-CH₂), 3.93–3.90 m (4H, 3-CH₂), 3.84–3.81 m (4H, 1'-CH₂), 3.68–3.65 m (4H, 4'-CH₂), 2.52–2.47 m (16H, NCH₂), 2.41–2.38 m (8H, NCH₂), 1.92 s (3H, 5-CH₃), 1.65-1.61 m (16H, CH₂), 1.48-1.45 m (8H, CH₂), 1.36–1.32 m (16H, CH₂), 1.01–0.98 m (24H, NCH₂CH₃). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 163.9, 162.7, 151.6, 151.5, 148.6, 146.3, 138.4, 121.9, 121.8, 110.0, 53.6, 52.8, 50.3, 50.1, 49.4, 47.1, 47.0, 45.8, 41.9, 41.3, 30.3, 30.2, 29.9, 29.1, 29.0, 27.7, 27.5, 26.9, 26.8, 26.5, 26.3, 26.2, 26.0, 25.3, 25.1, 23.1, 21.2,

16.7, 16.6, 13.2, 11.7, 11.6, 11.5. Mass spectrum (MALDI-TOF): m/z 1268.0 $[M - H]^+$ (calculated for C₆₉H₁₂₀N₁₆O₆: 1268.0). Found, %: C 65.32; H 9.59; N 17.57. C₆₉H₁₂₀N₁₆O₆. Calculated, %: C 65.27; H 9.53; N 17.65.

1,3-Bis(6-{4-[(1,3-bis{5-[decyl(diethyl)ammonio]pentyl}-6-methyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)methyl]-1H-1,2,3-triazol-1-yl}hexyl)-5methylpyrimidine-2,4(1H,3H)-dione tetrabromide (1). *n*-Decyl bromide, 0.73 g (3.0 mmol), was added to a solution of 1 g (0.79 mmol) of tetraamine 4 in 50 mL of acetonitrile, and the mixture was stirred at 50°C until the initial amine disappeared (TLC). The solvent was distilled off, the residue was distilled in water, the aqueous solution was treated with charcoal and filtered, and the solvent was distilled off. The residue was dissolved in chloroform, and the solution was dried over magnesium sulfate and evaporated. Yield 1.48 g (87%), off-white resinous material. IR spectrum. v, cm⁻¹: 2926, 2856, 1693 (C=O), 1640, 1466, 1050, 1026, 804, 770. ¹H NMR spectrum (CDCl₃), δ, ppm: 7.62 s and 7.58 s (2H, 4'-H), 7.07 s (1H, 6-H), 4.33-4.29 m (4H, 1'-CH₂), 3.92–3.84 m (8H, 3-CH₂, 1'-CH₂), 3.71–3.67 m (4H, 4'-CH₂), 3.51–2.29 m (32H, NCH₂), 1.91 s (3H, 5-CH₃), 1.85–1.40 m (104H, CH₂), 1.25-1.20 m (24H, NCH₂CH₃), 0.89-0.86 m (12H, CH₃). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 163.6, 162.1, 151.4, 150.0, 139.2, 110.9, 102.3, 57.5, 55.6, 52.4, 50.8, 48.3, 44.7, 31.9, 30.3, 29.7, 29.6, 29.4, 29.3, 28.4, 26.8, 26.4, 26.0, 25.7, 25.2, 24.8, 22.7, 16.5, 12.7, 8.3. Mass spectrum (MALDI-TOF): m/z 1998.4 [M – $2Br + 4H^{+}$ (calculated for $C_{109}H_{204}Br_4N_{16}O_6$: 1998.3). Found, %: C 60.82; H 9.48; Br 14.91; N 10.45. C₁₀₉H₂₀₄Br₄N₁₆O₆. Calculated, %: C 60.76; H 9.54; Br 14.83; N 10.40.

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