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Supramolecular water systems based on the new amphiphilic phosphacoumarins: synthesis, self-organizations and reactivity

Irina S. Ryzhkina, Lyaisan I. Murtazina, Andrey V. Nemtarev, Vladimir F. Mironov* and Alexander I. Konovalov

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, 420088 Kazan, Russian Federation. Fax: +7 843 273 1872; e-mail: mironov@iopc.kcn.ru

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Tensiometry, conductometry, dynamic light scattering, microelectrophoresis and kinetics of O-(4-nitrophenyl) O-ethyl chloromethylphosphonate hydrolysis in supramolecular water system based on 6-chloro-4-dodecyl-2-oxobenzo[e][1,2]oxaphosphinin-2-ol salts revealed that supramolecular nanoparticles structure of the system depended on counter-ion nature and substance concentration.

Surfactants, including phosphorus containing ones, are indispensable components in industry, in particular, pharmacy. A new synthesis of benzo[e][1,2]oxaphosphinines (phosphacoumarins) has been developed earlier.^{1–3} Herein this method was used for the preparation of new amphiphilic phosphacoumarins – 6-chloro-4-dodecyl-2-oxobenzo[e][1,2]oxaphosphinin-2-ol 1 and its sodium (2) and triethylammonium (3) salts,[†] which can serve as the potential surfactants and bioactive compounds as well as the model compounds for biomimetic and/or biocompatible nanosystems.



 † Self-assembling of the solutions of species 1–3 was studied by tensiometry, conductometry, dynamic light scattering, microeiectrophoresis (using Zetasizer Nano ZS, Malvern Instruments) under thermostatting of samples at 25 °C as described.7 Systems based on 2, 3 in the studied region of concentrations had a monomodal particle size distribution, which retained for 3 months, while the system based on $\mathbf{1}$ was stable only for 0.5 h. Relative errors in the measurement of electrical conductivity (χ) and surface tension (σ) of solutions did not exceed 1%, effective hydrodynamic diameter (D), electrokinetic potential (ζ) – 5%. Catalytic activity of supramolecular systems based on 2, 3 in the hydrolysis of O-(4-nitrophenyl) O-ethyl chloromethylphosphonate 4 was studied by recording 4-nitrophenolate emission (spectrophotometer Lambda 35, Perkin-Elmer) under the pseudo-first order conditions. Calculations of the observed reaction rate constants (k_{obs}) were performed according to the first-order equation. On the basis of the kinetic concentration dependences with an exit to the plateau in the micellar region of the compound 3 concentrations using the above-mentioned equation,¹² parameters of the micellar catalyzed reaction – reaction rate constants in micellar pseudophase (k_m) , constants of the substrate binding (K_b) and CMC were calculated.

Melting points were measured on a Boetius hot-stage and are uncorrected. NMR spectra were recorded on Bruker Avance-600 (¹H, 600 MHz; ¹³C, 150.9 MHz) and Bruker CXP-100 (³¹P, 36.48 MHz) spectrometers. The $\delta_{\rm H}$ and $\delta_{\rm P}$ values were determined relative to internal (HMDS) or external (H₃PO₄) standard, and the $\delta_{\rm C}$ values relative to the deuterated solvent signal. IR spectra were recorded on a Bruker Vector-22 instrument in Nujol.

In the present work new amphiphilic phosphacoumarins 1-3 were studied as self-organizing molecules in water solutions, and reactivity of supramolecular systems based on derivatives 2 and 3 in model hydrolysis of *O*-(4-nitrophenyl) *O*-ethyl chloromethylphosphonate 4 was investigated.

The surface tension isotherms for the water solutions of compounds 1-3 are shown in Figure 1. Inflection points on the concentration dependences of the surface tension of the solutions correspond to the critical micelle concentrations (CMC) (Table 1). Compound 1 is sparingly soluble in water, so its micelle-forming properties were studied in aqueous DMF (10 vol.%). The values of CMC for compounds 1-3, obtained by conductometry, an average size (effective hydrodynamic diameter) for the kinetically

Compound 1. A solution of tetradec-1-yne (26.7 ml, 0.109 mol) in CH₂Cl₂ (20 ml) was added dropwise to the mixture of 2,2,2-trichlorobenzo[1,3,2]dioxaphosphole (23.17 g, 0.094 mol), CH_2Cl_2 (30 ml) and hex-1-ene (7.9 g, 0.094 mol) under a stirring in an argon atmosphere. The reaction mixture was stirred for 30 min (15-20 °C), then the solvent, excess acetylene and the formed volatile products were removed in a vacuum (12 Torr, 120 °C). The yellow glass solid, 2,6-dichloro-4-dodecyl-2-oxobenzo[e][1,2]oxaphosphorinine, was obtained. This compound was dissolved in pentane (40 ml) and treated with water under stirring. The white precipitate formation gradually occurred. A precipitate was filtered off, pentane was separated and a viscous lower layer was treated with 90% aqueous acetone. Additional formation of compound 1 precipitate took place. The procedure was repeated four times. All solids were combined and dried in a vacuum (12 Torr). A total yield of compound 1 was 15.8 g (84%), mp 95–96 °C. IR (v/cm⁻¹): 460, 495, 504, 518, 554, 580, 600, 641, 668, 723, 775, 804, 837, 871, 1018, 1141, 1178, 1227, 1268, 1305, 1377, 1463, 1512, 1552, 1601, 1659, 2295, 2725, 2854, 2924, 3465. ¹³C NMR ([²H₆]DMSO): 115.31 [ddt (d), C³, ¹J_{PC³} 170.2 Hz, ${}^{1}J_{\text{HC}^{3}}$ 162.5 Hz, ${}^{3}J_{\text{HC}^{9}\text{CC}^{3}}$ 5.1 Hz], 151.72 [m (s), C⁴], 124.06 [m (d), C⁴a, ${}^{3}J_{\text{PCCC}^{4a}}$ 16.9 Hz], 126.58 [dd (s), C⁵, ${}^{1}J_{\text{HC}^{5}}$ 165.4 Hz, ${}^{3}J_{\text{HC}^{7}\text{CC}^{5}}$ 5.3 Hz], 128.25 [ddd (s), C⁶, ${}^{3}J_{\text{HC}^{8}\text{CC}^{6}}$ 11.4 Hz, ${}^{2}J_{\text{HC}^{7}\text{C}^{6}}$ 3.6 Hz, ${}^{2}J_{\text{HC}^{5}\text{C}^{6}}$ 3.6 Hz], 131.11 [dd (s), C⁷, ${}^{1}J_{\text{HC}^{7}}$ 168.1 Hz, ${}^{3}J_{\text{HC}^{5}\text{CC}^{7}}$ 5.3 Hz], 121.83 [dd (d), C⁸, ${}^{1}J_{\text{HC}^8}$ 165.2 Hz, ${}^{3}J_{\text{POC}^8}$ 6.7 Hz], 150.77 [dddd (d), C^{8a}, ${}^{2}J_{\text{POC}^8a}$ 7.6 Hz, ${}^{3}J_{\text{HC}^7\text{CC}^{8a}}$ 10.0 Hz, ${}^{3}J_{\text{PC}^5\text{CC}^{8a}}$ 10.0 Hz, ${}^{2}J_{\text{PC}^8\text{C}^{8a}}$ 2.9 Hz], 34.42 [tm (s), C⁹, ${}^{3}J_{\text{PCC}^9}$ 17.4 Hz], 32.24 [tm (s), C¹⁰], 29.7–30.0 [tm (s), C^{11–16}, ${}^{1}J_{\text{HC}}$ 125.2 Hz], 29.48 [tm (s), C¹⁷, ${}^{1}J_{\text{HC}^{17}}$ 126.3 Hz], 28.39 [tm (s), C¹⁸, ${}^{11}J_{\text{HC}^{18}}$ 125.8 Hz], 23.03 [tm (s), C¹⁹, ${}^{11}J_{\text{HC}^{19}}$ 124.4 Hz, ${}^{2}J_{\text{HCC}^{19}}$ 2.3], 14.26 [qtm (s), C²⁰, ${}^{1}J_{\text{HC}^{20}}$ 124.5 Hz, ${}^{2}J_{\text{HCC}^{20}}$ 3.1 Hz]. ${}^{31}\text{P}$ NMR ([${}^{2}\text{H}_{6}$]DMSO, 45 °C) δ : 5.53 (d, J 17.6 Hz). ¹H NMR ([²H₆]DMSO) δ : 0.85 (t, 3H, H²⁰, ³J_{HCCH} 5.9 Hz), 1.23–2.40 (m, 20H, H^{10–19}), 2.64 (t, 2H, H⁹, ${}^{3}J_{\text{HCCH}}$ 7.5 Hz), 6.22 (d, 1H, H³, ${}^{2}J_{\text{PCH}}$ 17.4 Hz), 7.22 (d, 1H, H⁸, ${}^{3}J_{\text{HC}^{7}\text{C}^{8}\text{H}}$ 8.8 Hz), 7.46 (br. d, 1H, H⁷, ${}^{3}J_{\text{H}^{8}\text{C}^{7}\text{H}}$ 8.8 Hz), 7.63 (br. s, 1H, H⁵). Found (%): C, 61.07; H, 8.75; Cl, 9.00; P, 8.59. Calc. for C₂₀H₃₀ClO₂P (%): C, 62.14; H, 7.86; Cl, 9.21; P, 8.05.



Figure 1 Isotherm of surface tension of aqueous solutions of (1) oxaphosphorinine 1 and its derivatives (2) 2 and (3) 3 (25 °C). Inset: (1) isotherm of surface tension of the aqueous solution of 3 and (2) change of particles diameters depending on concentration of solutions of compound 3.

active particles and their ζ -potentials, obtained at the concentration of 1×10^{-3} mol dm⁻³, are also given in Table 1.

Micelle formation in solution of acid 1 is stepwise, which is indicative of structural changes in the system. As this system is unstable in time, the study of its structural changes and micelle sizes was impossible.

Compound 2. Suspension of compound 1 (2.02 g, 0.005 mol) in Na₂CO₃ water solution of (0.21 g, 0.0025 mol, 15 ml) was heated until full dissolution of the solids. After 3 h white precipitate of compound $\mathbf{2}$ was formed. The precipitate was filtered off, washed with water and dried in air. Yield 1.8 g (89%), mp 216-217 °C. IR (v/cm⁻¹): 421, 442, 465, 478, 495, 525, 540, 588, 632, 682, 724, 738, 756, 786, 818, 831, 852, 881, 896, 9, 1083, 1132, 1178, 1213, 1269, 1308, 1342, 1377, 1464, 1552, 1603, 1643, 1754, 1890, 1909, 1959, 2168, 2283, 2672, 2726, 2958, 3072, 3364, 3576, 3610. ¹³C NMR ([²H₆]DMSO) δ: 123.71 [dm (d), C³, ${}^{1}J_{PC^{3}}$ 166.5], 142.84 [m (s), C⁴], 125.93 [m (d), C⁴a, ${}^{3}J_{PCCC^{4a}}$ 16.0 Hz], 124.96 [dd (s), C⁵, ${}^{1}J_{\text{HC}^{5}}$ 162.7 Hz, ${}^{3}J_{\text{HC}^{7}\text{CC}^{5}}$ 6.1 Hz], 125.26 [m (s), C⁶], 128.40 [dd (s), C⁷, ${}^{1}J_{\text{HC}^{7}}$ 166.2 Hz, ${}^{3}J_{\text{HC}^{5}\text{CC}^{7}}$ 6.1 Hz], 121.19 [dd (d), C⁸, ${}^{1}J_{\rm HC^{8}}$ 162.3 Hz, ${}^{3}J_{\rm POCC^{8}}$ 5.2 Hz], 155.18 [dddd (d), C^{8a}, ${}^{2}J_{\rm POC^{8a}}$ 7.0 Hz, ${}^{3}J_{\text{PCC}^{9}}$ 7.3 Hz, ${}^{3}J_{\text{PC}^{5}\text{CC}^{8a}}$ 7.3 Hz, ${}^{2}J_{\text{PC}^{6}\text{C}^{8a}}$ 3.6 Hz], 34.25 [tm (s), C⁹, ${}^{3}J_{\text{PCC}^{9}}$ 15.8 Hz], 31.81 [m (s), C¹⁰], 29.4–29.6 [tm (s), C^{11–16}], 29.17 [tm (s), C¹⁷], 28.34 [tm (s), C¹⁸], 22.55 [tm (s), C¹⁹, ${}^{1}J_{HC^{19}}$ 124.3 Hz, ²J_{HCC¹⁹} 3.5 Hz], 14.28 [qm (s), C²⁰, ¹J_{HC²⁰} 124.0 Hz]. ¹H NMR ([²H₆]DMSO) δ: 0.85 (t, 3H, C²⁰H₃, ${}^{3}J_{\text{HCCH}}$ 6.9 Hz), 1.2–1.5 (m, 20H, C^{10–19}H₂), 2.43 (t, 2H, C⁹H₂, ³J_{HCCH} 7.4 Hz), 5.97 (d, 1H, C³H, ²J_{PCH} 15.5 Hz), 6.90 (d, 1H, C⁸H, ${}^{3}J_{\text{HC}^{7}\text{C}^{8}\text{H}}$ 8.7 Hz), 7.16 (br. d, 1H, C⁷H, ${}^{3}J_{\text{HC}^{8}\text{C}^{7}\text{H}}$ 8.7 Hz), 7.32 (br. s, 1H, C⁵H). Found (%): C, 58.12; H, 7.93; Cl, 8.54; P, 8.04. Calc. for C₂₀H₂₉ClNaO₃P (%): C, 59.04; H, 7.18; Cl, 8.71; P, 7.61.

Compound 3. A mixture of compound 1 (2.19 g, 0.006 mol), dioxane (10 ml) and triethylamine (1.26 ml, 0.012 mol) was refluxed for 15 min. The white solid of compound 3 was obtained after evaporation of volatiles from the reaction mixture in air. Yield 2.7 g (93%), mp 35-36 °C. IR (v/cm⁻¹): 418, 449, 466, 514, 537, 573, 649, 667, 722, 755, 816, 836, 903, 976, 1039, 1081, 1133, 1179, 1216, 1342, 1378, 1399, 1467, 1553, 1601, 1645, 2492, 2676, 2737, 2851, 2921, 3439. ¹³C NMR ([²H₆]DMSO) δ: 121.56 [ddt (d), C³, ${}^{1}J_{PC^{3}}$ 166.3 Hz, ${}^{1}J_{HC^{3}}$ 163.4 Hz, ${}^{3}J_{HC^{9}CC^{3}}$ 5.6 Hz], 144.44 [m (s), C⁴], 125.15 [dd (d), C^{4a}, ${}^{3}J_{\text{PCCC}^{4a}}$ 15.8 Hz, ${}^{3}J_{\text{HC}^{8}\text{CC}^{4a}}$ 9.2 Hz], 125.02 [dd (s), C⁵, ${}^{1}J_{\text{HC}^{5}}$ 162.8 Hz, ${}^{3}J_{\text{HC}^{7}\text{CC}^{5}}$ 5.1 Hz], 125.82 [dm (s), C⁶, ${}^{3}J_{\text{HC}^{8}\text{CC}^{6}}$ 11.7 Hz], 128.87 [dd (s), C⁷, ${}^{1}J_{\text{HC}^{7}}$ 167.3 Hz, ${}^{3}J_{\text{HC}^{5}\text{CC}^{7}}$ 5.1 Hz], 121.16 [dd (d), C⁸, ${}^{1}J_{\text{HC}^{8}}$ 163.8 Hz, ${}^{3}J_{\text{POCC}^{8}}$ 5.6 Hz], 152.22 [m (d), C^{8a}, ${}^{2}J_{\text{POC}^{8a}}$ 7.1 Hz], 34.06 [tm (s), C⁹, ${}^{3}J_{\text{PCCC}^{9}}$ 15.8 Hz, ${}^{1}J_{\text{HC}^{9}}$ 125.1 Hz], 31.81 [tm (s), C¹⁰, ${}^{1}J_{HC^{9}}$ 124.1 Hz], 29.5–29.6 [tm (s), C^{11–15}, ${}^{1}J_{HC}$ 125.6–126.0 Hz], 29.34 [tm (s), C¹⁶, ${}^{1}J_{HC^{16}}$ 126.7 Hz], 29.24 [tm (s), C¹⁷, ${}^{1}J_{HC^{17}}$ 125.6 Hz], 28.07 [tm (s), C¹⁸, ¹J_{HC¹⁸} 125.6 Hz], 22.58 [tm (s), C¹⁹, ¹J_{HC¹⁹} 125.1 Hz], 14.25 [qm (s), C²⁰, ¹J_{HC²⁰} 124.6 Hz], 45.72 [t (s), NCH₂, ¹J_{HC} 140.4 Hz], 8.76 [q (s), Me, ${}^{1}J_{\text{HC}}$ 128.2 Hz]. ${}^{1}\text{H}$ NMR ([${}^{2}\text{H}_{6}$]DMSO) δ : 0.82 (br. s, 3H, C²⁰H₃), 1.12–1.45 (22H, C^{9–19}H₂), 2.94 (br. s, 6H, NCH₂), 3.67 (br. s, NH), 6.00 (d, 1H, C³H, ²J_{PCH} 16.1 Hz), 7.00 (br. d, 1H, C⁸H, ³J_{HC⁷C⁸H} 8.5 Hz), 7.5 (br. d, 1H, C⁷H, ${}^{3}J_{HC^{8}C^{7}H}$ 8.5 Hz), 7.37 (br. s, 1H, C⁵H). Found (%): C, 63.54; H, 9.87; Cl, 7.06; P, 6.82. Calc. for C₂₆H₄₅ClNO₃P (%): C, 64.25; H, 9.33; Cl, 7.29; P, 6.37.

Table 1 CMC, ζ -potentials and micelle size (*D*) of compounds 1–3 in water.

Com- pound	CMC (tensiometry)/ mol dm ⁻³	CMC (conductometry)/ mol dm ⁻³	D/nm	ζ/mV
1 ^a	1×10 ⁻⁴	1×10 ⁻⁴		
2	5×10 ⁻⁴	5×10 ⁻⁴	145	-55
3	7×10 ⁻⁵	7×10 ⁻⁵	106	-75.8

^a10% DMF, the system is unstable in time.

Micelle-forming properties of compound 1 and salts 2, 3 are different (Figure 1, Table 1). CMC of compound 2 is higher, while that of compound 3 is lower than that of compound 1. Structural features, particularly the presence of rigid aromatic and heterocyclic fragments in sodium salt 2, result in CMC (5×10^{-4} mol dm⁻³) which is 4 times lower than CMC of the anionic surfactant sodium deoxycholate (2×10^{-3} mol dm⁻³), which has also rigid fragment in its structure, and is significantly lower than CMC of widely used sodium dodecylsulfate detergent (SDS, 8×10^{-3} mol dm⁻³). Negative value of ζ -potential (-45 mV to -68 mV) of micelles 2 in the area of concentrations 5×10^{-4} -1×10⁻² mol dm⁻³ (Figure 2) points out that compound 2 is anionic micelle-forming surfactant.

For better understanding of micelle formation processes in solutions of compound 2, it is important to observe concentration changes of D and ζ -potential of particles, especially in premicellar area. As judged from surface tension isotherm appearance, aggregation of molecules in the system is expected. Figure 2 represents concentration dependences of surface tension of solutions of **2**, *D* and ζ -potential of particles formed. Comparison of data obtained by different experimental methods evidence that in premicellar interval of concentrations 5×10⁻⁵-3×10⁻⁴ mol dm⁻³ with maximum in the area of 1×10^{-4} mol dm⁻³, associates of salt 2 are formed and rearranged in the solution; their size changes from 100 to 200 nm depending on concentration of compound 2. Taking into account low concentrations of salt 2 and large sizes of particles, it can be suggested that water structures similar to the hydrated fullerene nanoparticles of 70 nm in size at concentration 1×10⁻⁴ mol dm⁻³ participate in the particles formation.⁴ Similar results were obtained for analogous concentration range of SDS solutions⁵ wherein a maximum light scattering coefficient connected with the structural changes of the water nearby aggregates or SDS molecules was detected.

Concentration-dependent rearrangements of nanoassociates of compound **2** are accompanied by changing of the ζ -potential negative values. A nonlinear concentration dependence of size and ζ -potential of nanoassociates in the solutions of compound **2** in the region of 1×10^{-5} - 3×10^{-4} mol dm⁻³ looks like that of size^{6,7} and ζ -potential of the nanoassociates detected in the solutions of the 'melaphen' plant growth regulator and ichphan C-10 functional cationic surfactant within the concentration range



Figure 2 Concentration dependences of (1) associates diameters, (2) surface tension and (3) ζ -potential of nanoparticles in aqueous solution of compound 2.

of $1 \times 10^{-20} - 1 \times 10^{-4}$ mol dm⁻³. Probably negative ζ -potential values, irrespective of the dissolved substance nature, is characteristic of the nanoassociates formed together with water structures in the region of the low concentrations. This follows from the fact that hydrated fullerene nanoparticles have also negative surface charge.⁸ Concentration dependences of surface tension, *D* and ζ -potential of particles come to a plateau on reaching CMC, confirming a formation of the micelles of about 130–140 nm in size.

Replacement of inorganic counter-ions Na⁺ by organic Et₃N⁺H leads to a decrease in CMC of the compound 3 solutions in comparison with those of 1 and 2. Triethylammonium salt 3 has CMC of 7×10⁻⁵ mol dm⁻³, specific to the zwitterionic and nonionic surfactants. It can be suggested that organic counter-ions are in a bound state, which gives to compound 3 specific micelleforming properties due to the absence of signified charge on a micelle surface. Inset in Figure 1 shows that the size of nanoassociates of compound 3 (160 nm) in a premicellar region is larger than the size of micelles (106 nm), which is analogous to compound 2. However, in solutions of compound 3, contrary to solutions of 2, in the studied region of concentrations the nanoassociates sizes and changes of ζ -potential do not increase. Therefore, concentration-defined rearrangements of nanoassociates in the solutions of species 2 and 3 is determined by counter-ion nature.

According to X-ray analysis, structure of compound 1 in solid phase represents bilayers packed by a zigzag manner and formed due to hydrophobic interactions of the aromatic rings, hydrocarbon substituents and hydrogen bonds between main groups of molecules 1.9 Taking into account these data, it can be supposed that micelles of molecules 2 and 3 represent bilayers formed by anionic skeleton of 1, cations and 'interlayers' of the hydrated water, which provides them sufficiently large sizes similar to myelines.¹⁰ Note that particles of 4 nm in size are observed together with those of more than 100 nm in size in the region of 10⁻² mol dm⁻³ exceeding CMC by two orders; and this agrees with well known data on a concentration-dependent change of the surfactants sizes for their organized assemblies. High negative values of the ξ -potential of particles 3, which are equal -(65-90) mV in the concentration range of $10^{-4}-10^{-3}$ mol dm⁻³ can be accounted for by the fact that electrophoresis-induced external electric field results in dissociation of triethylammonium groups and formation of micelles with a high negative surface charge ('nude' micelles), which are probably slightly ionized ('dressed' micelles) under ordinary conditions.¹¹

Figure 3 exhibits data on kinetics of hydrolysis of compound **4** in premicellar and micellar regions of concentrations for species



Figure 3 Observed rate constant (k_{obs}) of hydrolysis in aqueous solution of (1) **3**, (2) **2** and (3) CTAB as a function of their concentration, 25 °C, pH 8. Inset: (1) observed rate constant (k_{obs}) of hydrolysis of **4** and (2) particles size in aqueous solution of **2** as a function of concentration, 25 °C, pH 8.

2 and **3** as well as solutions of cationic cetyltrimethylammonium bromide (CTAB). Solutions of the compounds effectively catalyze hydrolysis of *O*-(4-nitrophenyl) *O*-ethyl chloromethylphosphonate under mild conditions: a reactivity of the supramolecular system **3** exceeds approximately by one order that of CTAB (the latter is known to be a good catalyst of carboxylic and phosphoric esters hydrolysis¹²). This confirms that micelles of **3** contain Et₃N⁺H groups in bound state, which can catalyze hydrolysis of compound **4**.

In spite of the negative charge of micelle 2, which usually results in inhibition of carboxylic and phosphoric esters hydrolysis, reactivity of system 2 in the region of concentrations over 1×10^{-3} mol dm⁻³ is comparable with that for CTAB which can mean an assistance of functional groups of molecule 2 in hydrolysis. It is interesting that the reactivity of system 2 in the region of low concentrations within $5 \times 10^{-5} - 5 \times 10^{-4}$ mol dm⁻³, where nanoassociates are formed (Figure 3, inset), exceeds substantially the reactivity of micelles 2, 3 and CTAB formed in a higher concentrations region. This additionally confirms that the reactivity of supramolecular system is determined mainly by the structure and properties of supramolecular particles. High reactive supramolecular nanoassociates are formed and undergo the structural rearrangements in the studied system 2 in the narrow range of low concentrations. When reagent concentration in solution increases these nanoassociates transform into micellar structures, which possess lower reactivity.

Tensiometry, conductometry, dynamic light scattering, microelectrophoresis and kinetic data evidence that compounds 1-3are surfactants; micelle-forming properties and reactivity of solutions of compounds 2, 3 are determined by supramolecular nanoparticles structure which depends on counter-ion nature and substance concentration.

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