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Magnesium Octa(benzo-15-crown-5)phthalocyaninate in the Sodium Dodecyl Sulfate Solutions: A Study Using Electron and ^{1}H NMR Spectroscopy

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Abstract—The behavior of magnesium octa(benzo-15-crown-5)phthalocyaninate in water medium in the presence of sodium dodecyl sulfate was studied using both electronic and ^{1}H NMR spectroscopy, including the method of two-dimensional ^{1}H–^{1}H correlation NOESY. In the microheterogeneous environment of the $CH_3(CH_2)_{11}OSO_3Na$ solutions at the concentrations of the latter close to the CMC the phthalocyanine is in monomeric form, while at the concentration less than the critical micelle-formation concentration it becomes a dimer or even more aggregated. The results of the NMR spectroscopic investigation indicate that magnesium octa(benzo-15-crown-5)phthalocyaninate preferrably binds to the $CH_3(CH_2)_{11}OSO_3Na$ micelle in the hydrophobic region of the latter.

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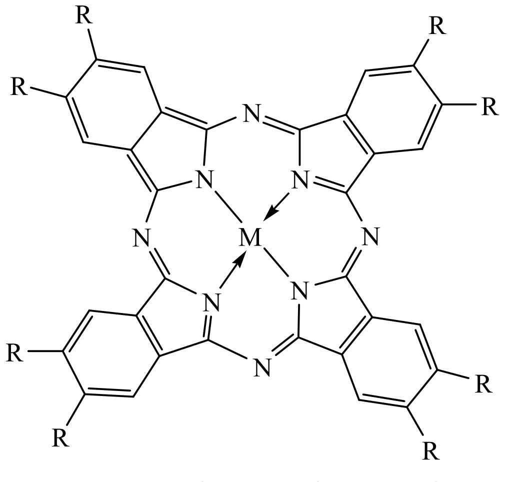
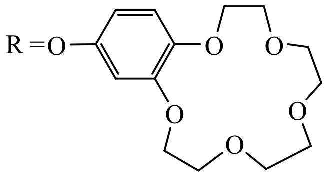
Owing to their complexing, electrophysical, optical, and other properties, phthalocyanines and their supramolecular aggregates are used in devices of molecular electronics and in chemical sensors, in catalysis, as well as in biology and medicine, in particular, as reagents for diagnostics and photosensitizers in photodynamic therapy. Attaching peripheral substituents to the phthalocyanine molecules affects markedly their physical and chemical characteristics. In particular, the crown ethers, both fused [1] and attached to the macrocycle via an oxygen bridge [2] not only increase solubility, but also contribute to the organization of the phthalocyanine molecules as the ensembles involving a cation as a *guest*. So, nickel (**Ib**) and cobalt (**Ic**) octa(benzo-15-crown-5)phthalocyaninates in the presence of cations K^+ (or Bu_4N^+) and Na^+ can be dissolved in propylene carbonate with the formation of dimers and monomers, respectively, and can form dimers in aqueous solutions of KCl [3].



M = $2H^+$ (**Ia**), Ni^{2+} (**Ib**), Co^{2+} (**Ic**), Mg^{2+} (**Id**);



The crown-containing phthalocyanines are soluble in aqueous solutions of sodium dodecyl sulfate [4],

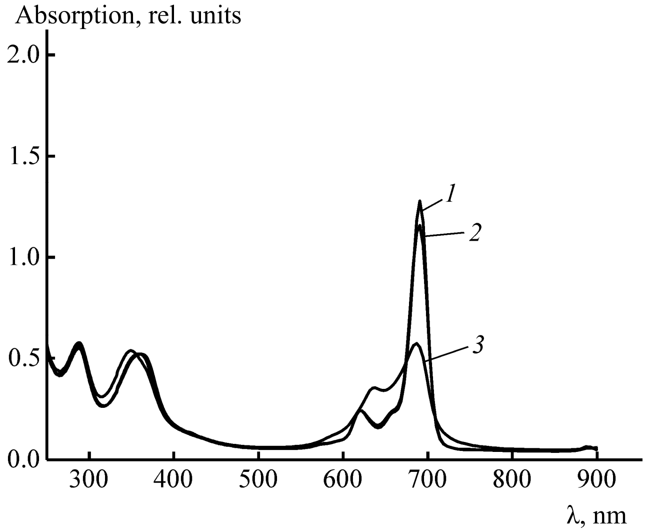


Fig. 1. EAS of magnesium octa[(4'-benzo-15-crown-5)-oxy]phthalocyaninate (**Id**) in dichloromethane (*1*) and a mixed solvent, $C_2H_5OH–CH_2Cl_2$ at the ratio by volume 1:1 (*2*) and 4:1 (*3*). Concentration of **Id** in all these solutions is 7.7×10^{-6} M.

[$CH_3(CH_2)_{11}OSO_3Na$], a representative of anionic surfactants, carrying a polar *head* and nonpolar (hydrophobic) *tail*. A change in properties of solutions of a surfactant, including the reduction of its surface tension and increased ability to solubilize hydrophobic molecules, occurs at critical micelle concentration (CMC). When the concentration of sodium dodecyl sulfate is near the CMC, the compound **Ia** occurs in solution in a monomeric form, while at the concentration of sodium dodecyl sulfate much less than the CMC it exists as a dimer [4]. The size of the cation of the solubilizing component and the presence in the latter of hydrophobic groups affect the form of existence the crown-containing phthalocyanine in water environment.

In this work, by an example of magnesium octa(benzo-15-crown-5)phthalocyaninate, we attempted to characterize the phthalocyanine environment in micellar solution of sodium dodecyl sulfate and the ability of inclusion of crown-containing phthalocyanine in the anionic micelles. In the study we used electronic spectroscopy in UV and visible regions and ^{1}H NMR spectroscopy, including two-dimensional ^{1}H–^{1}H correlation NOESY, which can be used to establish the interacting protons in a molecule or in a molecular ensembles like micelles.

The electron absorption spectra (EAS) were obtained for the magnesium octa(benzo-15-crown-5) phthalocyaninate in aqueous solutions of sodium dodecylsulfate and in a weakly polar organic solvent dichloromethane (ε_0 8.9). Comparison of the spectral properties of these solutions made it possible to characterize the environment of compound **Id** in the presence of anionic surfactant and the nature of the interaction in the system of phthalocyanine–$CH_3(CH_2)_{11}OSO_3Na$.

Study of properties of Id in organic solvents. Magnesium 2,3,9,10,16,17,23,24-octa[(4'-benzo-15-crown-5)oxy]phthalocyaninate was obtained by prolonged refluxing 4,5-bis[(4'-benzo-15-crown-5)oxy]-1,2-dicyanobenzene and magnesium metal in dry butanol. The EAS of **Id** in dichloromethane is typical for the monomeric phthalocyanine (Fig. 1, curve *1*). It comprises a series of bands in the UV and visible regions: a broad *N*-band at 288 nm, a Soret band at 360 nm, and a strong *Q*-band at 690 nm ($\varepsilon = 1.64\times10^5$ l mol^{-1} cm^{-1}) with a satellite of lower intensity at the shorter wavelengths. Half-width of the *Q*-band is ~530 cm^{-1}. In the concentration range 2.5×10^{-6} to 2.5×10^{-5} M the solutions of **Id** do not deviate from the Bouguer–Lambert–Beer law. Like the case of compound **Ic** [3], the tetraoctylammonium bromide does not affect the character of the **Id** spectrum (1.35×10^{-5} M) in CH_2Cl_2 solution at the tetraoctylammonium bromide: phthalocyanine **Id** ratio from 20:1 to 40:1, that is, the effect of the medium polarization at these concentrations does not play a significant role. In the mixed solvent ethanol–dichloromethane ($C_2H_5OH:CH_2Cl_2$ = 1:1 by volume), the spectrum of **Id** changed little compared with that in CH_2Cl_2 (Fig. 1, curve *2*). Further increase in the C_2H_5OH concentration leads to a marked decrease in the intensity of the *Q*-band in the region of the monomer absorption, which, together with its broaden-ing and a blue shift, indicates the aggregation of **Id** molecules (Fig. 1, curve *3*). Note that the aggregation of **Id** in the mixed solvent requires higher alcohol content ($C_2H_5OH:CH_2Cl_2$ ratio) compared with the case of **Ic** [3].

Study of the properties of Id in water medium. A feature of the crown ethers is the presence of both hydrophobic (hydrocarbon) and hydrophilic fragments in the molecule. Nevertheless the crown-containing phthalocyanine **Id**, like the other phthalocyanines without polar groups in the macrocycle, is insoluble in water. On the other hand, the presence of a cavity formed by oxygen atoms of crown ether facilitates interactions of the *guest–host* type. This favors dissolution of the phthalocyanine molecules in a polar environment with an alkali metal cation acting as a *guest* [3].

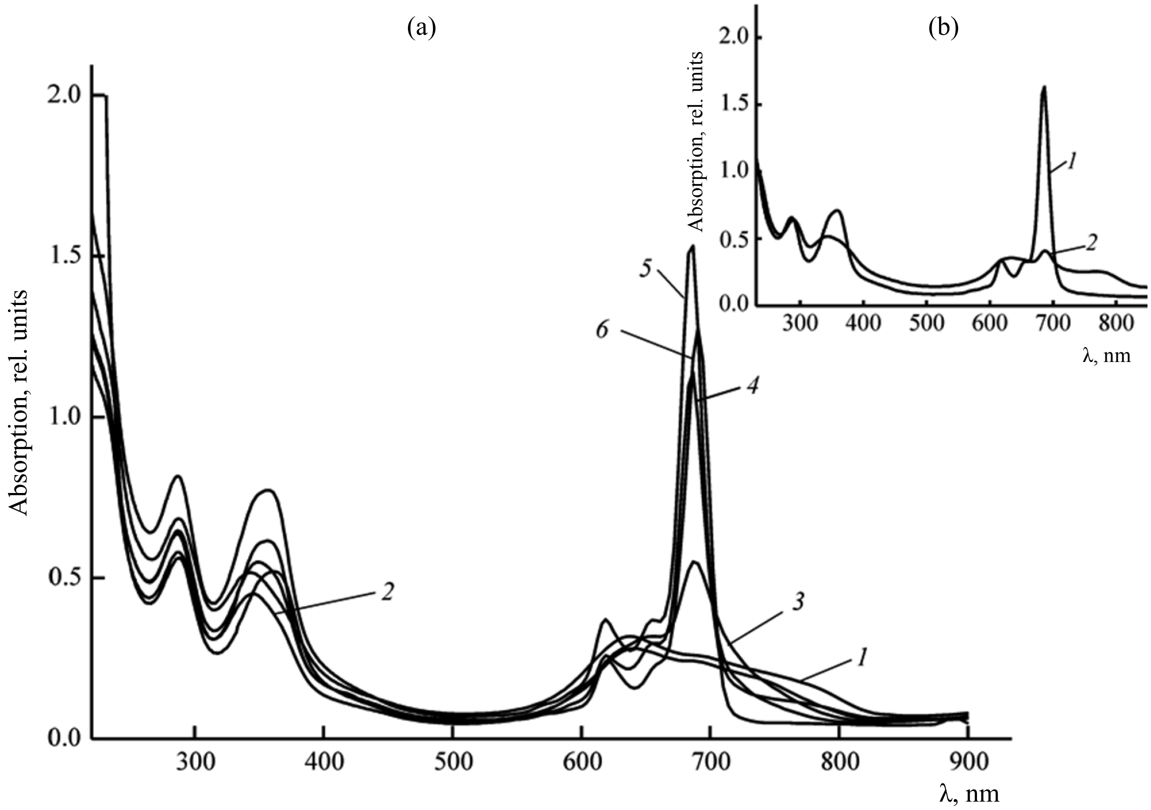


Fig. 2. Absorption spectra of **Id**: (a) in aqueous solution of sodium dodecyl sulfate (*1*–*5*) and in CH_2Cl_2 (*6*). [**Id**] = 8.8×10^{-6} and 7.7×10^{-6} M in the solutions of $CH_3(CH_2)_{11}OSO_3Na$ and CH_2Cl_2 , respectively, $[CH_3(CH_2)_{11}OSO_3Na] = 0.46\times10^{-3}$ (*1*), 1.85×10^{-3} (*2*), 5.1×10^{-3} (*3*), 6.9×10^{-3} (*4*), 9.7×10^{-3} (*5*) M; (b) in the presence of $CH_3(CH_2)_{11}OSO_3Na$ (*1*) and $CH_3(CH_2)_{15}(CH_3)_3NBr$ (*2*) in water medium, [**Id**] = 9.2×10^{-5} (*1*) and 1.1×10^{-4} M (*2*), $[CH_3(CH_2)_{11}OSO_3Na] = 2.25\times10^{-2}$, $[CH_3(CH_2)_{15}(CH_3)_3NBr] = 8.6\times10^{-3}$ M.

Like other crown-containing phthalocyanines [4], **Id** is soluble in aqueous solution of sodium dodecyl sulfate. At the concentrations below the CMC, the sodium dodecyl sulfate molecules occur in solution as monomeric solvated species, and when the sodium dodecyl sulfate concentration approaces the CMC they form micelles. The characteristics of these micelles, including size, value of the CMC, and aggregation number are well known [5, 6]. The number of molecules of ionic surfactant in a micelle is determined by the electrostatic repulsion of the polar *heads*, and in the case of sodium dodecyl sulfate it is 60–70 units for spherical micelle at 25°C [6].

Diameter of Na^+ ion (1.9 Å) corresponds to the diameter of the cavity of 15-crown-5 (1.7–2.2 Å). According to the principle of geometric correspondence [7], the presence of this ion will not contribute to the cation-induced aggregation of phthalocyanine. The crown-containing phthalocyanine compounds **Ib** and **Ic** remain insoluble in aqueous solutions of NaCl, despite the closeness of the size of Na^+ and the crown ether cavity [3]. Compound **Ia** is slowly dissolved in an aqueous solution of NaOH (0.019 M) to form, according to the absorption spectra, aggregated structures of the phthalocyanine. Cobalt phthalocyanine, which does not include the crown groups in the macrocycle, is practically insoluble in water solutions at the concentrations of sodium dodecyl sulfate even much higher than the CMC.

Figure 2*a* shows the absorption spectra of **Id**–sodium dodecyl sulfate solutions at varying concentrations of the latter, including those corresponding to the boundary conditions, when the sodium dodecyl sulfate concentration is much below the CMC or close to it (curves *1* and *5*, respectively). The shape and position of the phthalocyanine *Q*-band (686 nm) in the spectrum *5* and the comparison of this spectrum with the spectrum of solution in dichloromethane (Fig. 2a, curve *6* and Fig. 1, curve *1*), indicate that at the concentration of sodium dodecyl sulfate close to CMC (8.2×10^{-3} M), the magnesium octa(benzo-15-crown-5)-phthalocyaninate exists in the micellar solution as a monomer. This state persists practically also at the **Id** and sodium dodecyl sulfate concentrations 1.0×10^{-4}

and 2.25×10^{-2} M, respectively[1]. Comparing the spectra of **Id** in the presence of anionic and cationic surfactants, sodium dodecyl sulfate and hexadecyltrimethylammonium bromide [$CH_3(CH_2)_{15}N(CH_3)_3Br$], respectively (Fig. 2b), shows the difference in the state of phthalocyanine in these solutions . The state of the phthalocyanine in the **Id**–sodium dodecyl sulfate system at the varied concentration of the latter was monitored by diluting the solution at the sodium dodecyl sulfate concentration near the CMC.

The spectra in Fig. 2a show that the position of *N*-band with a maximum at 288 nm remains unchanged at the sodium dodecyl sulfate concentration in the range 4.6×10^{-9}–7×10^{-3} M (or higher). At lower concentrations of $CH_3(CH_2)_{11}OSO_3Na$, the Soret band suffers a slight blue shift relative to its position in the spectrum of **Id** solution in dichloromethane where **Id** is a monomer. When the sodium dodecyl sulfate concentration falls to 4.6×10^{-4} M, that is, in the absence of micelle formation, the visible region does not contain clearly defined (individual) *Q*-band of the dimeric form of the phthalocyanine. The absorption band (620–820 nm) is rather complex (Fig. 2a, curve *1*), suggesting the presence of various aggregated forms of phthalocyanine, including, possibly, the nanoparticles. The shift of the *Q*-band to longer wavelengths is observed usually for porphyrins [8] and phthalocyanines [9] at the transfer them from a weakly polar (or apolar) environment to the polar medium, due to the stacking interactions.

Note that in practice an attempt to solubilize compound **Ic** with hexadecyltrimethylammonium bromide led only to the formation of aggregates [4]. Diameter of the polar head of hexadecyltrimethylammonium bromide is ~5.8 Å, and its concentration 8.6×10^{-3} M is significantly above the CMC in water (1.0×10^{-3} M). The phthalocyanine **Id** behaves similarly (Fig. 2b, curve *2*). It is known that in the spectrum of the crystalline complex $MgPc(H_2O)(C_2H_5)_3N$ together with absorption at 615–690 nm, a strong band occurs in the near infrared region, at 800 nm [10]. In the spectrum of vanadyl phthalocyanine VOPc with an average particles size 2.3 nm in the presence of hexadecyltrimethylammonium bromide an absorption is observed at 550–900 nm [11]. Thus, the aggregation of crown-containing phthalocyanine in aqueous solutions of cationic surfactants with the diameter of the polar head much larger than the diameter of the cavity of phthalocyanine crown fragment indicates that hydrophobic interactions alone are not enough to solubilize **Id** with the formation of a micelle-bound monomer.

Unlike the **Id**–hexadecyltrimethylammonium bromide (Fig. 2b), in the micellar solution at a concentration of sodium dodecyl sulfate slightly higher than CMC the phthalocyanine **Id** is in monomeric form (Fig. 2a, curve *5*). Therewith, the *Q*-band (686 nm) is slightly shifted toward shorter wavelengths relative to its position in the absorption spectrum of solution in methylene chloride (690 nm). Similar changes in λ are typical also of the monomeric forms of **Ia** and **Ic** in the micellar solutions of sodium dodecyl sulfate [4]. The values of molar extinction coefficient ε are 1.7×10^5 and 1.64×10^5 l mol^{-1} cm^{-1} for micellar and CH_2Cl_2 solutions of **Id**, respectively. The observed proximity of the spectral characteristics (the values of ε, position of the absorption bands and the ratio of their optical densities), and virtual absence of the **Id** aggregation indicates that the phthalocyanine surrounding in the micellar solutions of sodium dodecyl sulfate is close in polarity to dichloromethane. This suggests that phthalocyanine is bound by the micelle and forms a micelle-like complex **Id**–sodium dodecyl sulfate in the course of the **Id** solubilization at the concentration of sodium dodecyl sulfate equal to or higher than the CMC. Therewith, the phthalocyanine crown fragments bearing a positive charge as a result of coordination of Na^+ being arranged near the OSO_3^- groups of sodium dodecyl sulfate in the micelle aqueous layer, the Stern layer, which comprises, along with the polar *heads*, also the counterions and the molecules of hydration water. At low concentrations of sodium dodecyl sulfate aggregation of **Id** occurs (Fig. 2). Similar behavior of phthalocyanine is observed at changing the medium polarity (Fig. 1, curve *3*, $C_2H_5OH:CH_2Cl_2 = 4$). The polarity of the Stern layer is characterized as an intermediate between that of water and hydrocarbons (“alcohol-like”) [12]. In a mixed solvent, $H_2O:C_2H_5OH = 1:4$, the presence of the monomeric form **Id** is detected at a concentration of sodium dodecyl sulfate ~0.1 M, which is significantly higher than the CMC in aqueous medium.

Figure 3 shows the changes in optical density at λ = 686 nm of **Id** solutions depending on the sodium dodecyl sulfate concentration. At the concentrations above CMC ([**Id**] = const), the optical density of the solution remains almost unchanged in the range of 1×10^{-2} to 6×10^{-2} M. The effect of the sodium dodecyl sulfate concentration on the state of **Id** clearly demon-

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[1] Effect of phthalocyanine on the CMC value is not considered in this work.

strates the importance of micelle formation at the solubilization of phthalocyanine in water environment. A decrease in optical density of the solution **Id**–sodium dodecyl sulfate at the surfactant concentration above CMC2 can apparently be attributed to the changes in the structure (size and shape) of micelles and the stability of micelle-bound phthalocyanine complex, respectively.

Effect of electrolytes on the state of Id in aqueous mixtures Id–sodium dodecyl sulfate. The EAS of the **Id**–sodium dodecyl sulfate solution at 686 nm remains practically the same upon dilution with 0.64% aqueous solution of sodium carboxymethylcellulose or water (Fig. 4a). This fact suggests that the presence of the sodium carboxymethylcellulose polyelectrolyte does not affect the state of **Id** at low (5.0×10^{-4} M) concentration of sodium dodecyl sulfate. The increase in the concentration of Na^+ (increase in the ionic strength) does not prevent the stack aggregation of **Id** at the sodium dodecyl sulfate concentrations much below the CMC, and it does not reduce the value of the latter. Such behavior of **Id** in polyelectrolyte solutions at low surfactant concentration demonstrates that the **Id** solubilization in aqueous solution shows the necessity in the synergism of non-covalent interactions of different types.

Another pattern is observed when the micellar solution of **Id** in aqueous solution of sodium dodecyl sulfate is diluted with potassium chloride (Fig. 4b). Comparing the spectra *1* and *2* (dilution with aqueous KCl and H_2O, respectively, at the unchanged sodium dodecyl sulfate concentration, 4.6×10^{-4} M) shows that in solutions with the sodium dodecyl sulfate concentration much below the CMC, the presence of KCl (0.058 M) affects significantly the state of **Id**. By the shape, the spectrum *1* is almost identical with the spectrum of **Id** in solution with the sodium dodecyl sulfate concentration 5.1×10^{-3} M (Fig. 2a, curve *3*). As seen, the monomer band intensity decreases while simultanously the optical density increases in the region of phthalocyanine dimer, that is, the peak of the monomer characteristics of **Id** in the sodium dodecyl sulfate micellar solution suffers splitting. As a result, despite the different concentrations of sodium dodecyl sulfate in the **Id**–sodium dodecyl sulfate and **Id**–sodium dodecyl sulfate–KCl solutions (5.1×10^{-3} and 4.6×10^{-4} M respectively), the spectral pattern indicates little changes in the state of the phthalocyanine. The electrolytes like KCl reduce the value of CMC of sodium dodecyl sulfate [6], however, K^+ (diameter 2.66 Å) contributes to the cation-induced dimerization of phthalocyanine with the formation of cofacial dimers [1, 3]. The balance of these factors can lead to a change in the state of **Id** in the sodium dodecyl sulfate–KCl system, which is accompanied by the corresponding changes in the EAS. Thus, the data obtained show, on the one hand, the diversity of interactions in the **Id**–sodium dodecyl sulfate system, and, on the other hand, demonstrate the influence of micelle formation on the form of existence of **Id** in water environment.

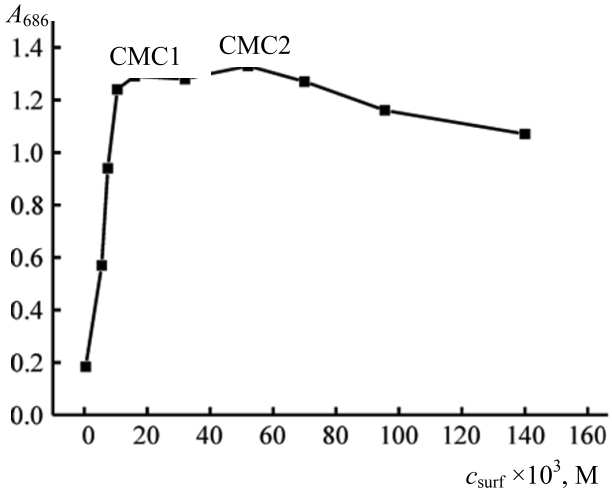

Fig. 3. Change in optical density of the **Id**–sodium dodecyl sulfate solution at λ = 686 nm vs the concentration of sodium dodecyl sulfate, [**Id**] = 8.9×10^{-6} M.

Study of the Id–sodium dodecyl sulfate micellar solutions with the use of ^{1}H NMR spectroscopy. The analysis of the EAS of **Id** in aqueous micellar solution of sodium dodecyl sulfate with the surfactant concentration equal to or above CMC suggests that at the magnesium octa(benzo-15-crown-5)phthalocyaninate solubilization with sodium dodecyl sulfate a micelle-bound monomer is formed, and this process comprises the non-covalent interactions of various types, including *guest–host*, electrostatic and hydrophobic.

When a phthalocyanine with crown fragments in the macrocycle coordinates Na^+ at the solubilization in an aqueous solution of sodium dodecyl sulfate, it becomes a charged species. The possibility of finding phthalocyanine in the micelle bulk is governed by the hydrophobicity of the macrocycle, and its appearance in the micelle shell, by the Coulomb interactions of charged species. It is known that 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) interacts with anionic sodium dodecyl sulfate micelles only through the formation of a complex with the Na^+ ion [13]. An increase in hydrophobicity at the introduction of

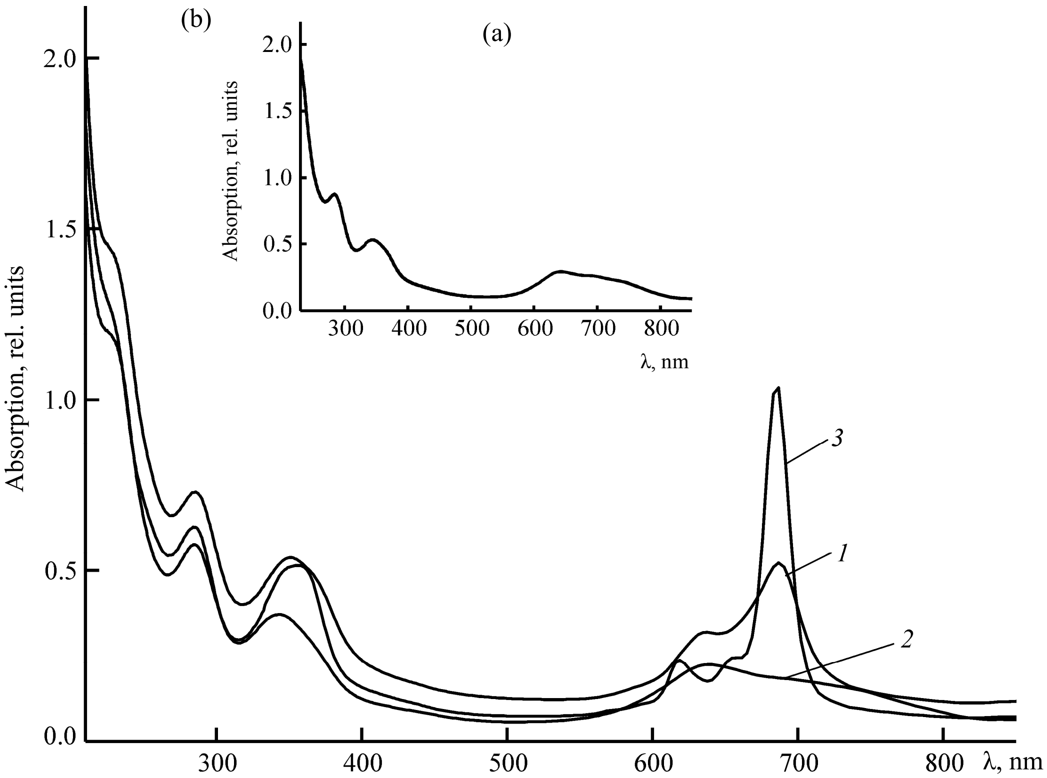

Fig. 4. The absorption spectra of **Id**–$CH_3(CH_2)_{11}OSO_3Na$ system after diluting: (a) with aqueous 0.64% solution of sodium carboxymethylcellulose or water, [**Id**] = 8.8×10^{-6}, [$CH_3(CH_2)_{11}OSO_3Na$] = 5.0×10^{-4} M, (b) with aqueous 0.058 M KCl (*1*), water (*2*) and 0.0097 M sodium dodecyl sulfate (*3*), [**Id**] = 8.8×10^{-6} M, [$CH_3(CH_2)_{11}OSO_3Na$] = 4.6×10^{-4} M (spectra *1* and *2*).

substituents leads to the distribution of the 18-crown-6 molecules between the shell and the inner region of the micelles, which is a consequence of electrostatic and hydrophobic interactions, respectively [14].

In order to identify by the ^{1}H NMR method, which is widely used for the study of organized supramolecular ensemblies of molecules, the site of **Id** binding with sodium dodecyl sulfate micelle, we carried out analysis of the chemical shifts for all groups of sodium dodecyl sulfate. The table lists the sodium dodecyl sulfate proton chemical shifts in the absence and in the presence of **Id**.

Figure 5 shows the ^{1}H NMR spectrum for the system of sodium dodecyl sulfate–**Id** in D_2O. The signals of the aromatic protons of **Id** are located in the region of 6.0–9.5 ppm, and the signals of CH_2 groups of the crown fragment, at 3.4–4.5 ppm. The signals of sodium dodecyl sulfate protons are broadened compared with the spectra of the sodium dodecyl sulfate solution in the absence of **Id**, indicating the interaction of phthalocyanine with the molecules of sodium dodecyl sulfate. The table shows that the resonance of the protons of all groups of sodium dodecyl sulfate in the presence of **Id** are shifted upfield. This can be due to shielding the hydrogen atoms of sodium dodecyl sulfate due to the influence of the aromatic rings. The increase in the **Id** concentration results in growing of Δδ values of the sodium dodecyl sulfate proton signals. In addition, the change in the proton chemical shifts of methylene and methyl groups of the sodium dodecyl sulfate hydrocarbon chain is larger than the shift of the protons of α- and β-CH_2 groups adjacent to the polar *head*. This change in δ and its direction may be an indication of the interaction of **Id** with all groups of sodium dodecyl sulfate.

In accordance with the above suggestions about the site of phthalocyanine binding with sodium dodecyl sulfate micelle at the solubilization, we can assume two models of a species that includes **Id**, namely, the localization of phthalocyanine either in the micelle bulk or at its the periphery in the charged interfacial boundary region. To realise which of the assumed models is more correct, we performed a two-dimensional NMR ^{1}H –^{1}H NOESY experiment based on the Overhauser effect. Figure 6 shows the resulting

Parameters of ^{1}H NMR spectra of sodium dodecyl sulfate and **Id**–$CH_3(CH_2)_{11}OSO_3Na$ system[a]

[**Id**], M	$\overset{\omega}{C}H_3(CH_2)_9\overset{\beta}{C}H_2\overset{\alpha}{C}H_2OSO_3Na$							
	α-CH_2		β-CH_2		(–CH_2–)$_9$		ω-CH_3	
	δ	Δδ	δ	Δδ	δ	Δδ	δ	Δδ
0	3.963		1.619		1.244		0.824	
0.00027	3.957	–0.006	1.613	–0.006	1.235	–0.009	0.815	–0.009
0.0023	3.948	–0.015	1.603	–0.016	1.200	–0.044	0.780	–0.044

[a] The δ values were measured using the signal of residual protons in D_2O (4.71 ppm) of the solution of pure $CH_3(CH_2)_{11}OSO_3Na$. The values of δ for the sodium dodecyl sulfate in the presence of compound **Id** were determined soon after the registration of the spectrum of pure $CH_3(CH_2)_{11}OSO_3Na$ in D_2O, maintining a constant magnetic field. Similar Δδ values were obtained using the TMS as an external reference. In all solutions, the $CH_3(CH_2)_{11}OSO_3Na$ concentration in D_2O was 0.32 M.

two-dimensional spectrum. Rectangle with dotted lines emphasizes a region of the spectrum which shows the signals indicating the interaction of aromatic hydrogen atoms of phthalocyanine with the $(CH_2)_9$ protons of sodium dodecyl sulfate. The existence of such an interaction indicates that the preferred model is that of binding **Id** with the anionic sodium dodecyl sulfate micelle in the hydrophobic region of the latter. In the second model that assumes binding of phthalocyanine in the interfacial boundary region of the micelle, the hydrogen atoms of the aromatic rings are too distant from the $(CH_2)_9$ groups of sodium dodecyl sulfate. In addition, phthalocyanine acquired a positive charge (maximum 8) during the solubilization, and its binding by anionic micelles of sodium dodecyl sulfate in the aqueous layer should lead to more significant changes in the proton chemical shifts of α- and β-CH_2 groups (as a result of reducing the layer polarity) than it was found.

According to the ^{1}H NMR data, at the interaction of water-soluble tetrasulfoporphyrins with cationic micelles of hexadecyltrimethylammonium bromide a large downfield shift is observed of the protons of α- and β-CH_2 groups of the surfactant, while for the protons of other groups a slight upfield shift is noted. This was interpreted in the sense that the interactions leading to binding the molecules of the macrocyclic compounds with hexadecyltrimethylammonium bromide micelles were predominantly electrostatic [15]. The same type of interaction between the cation $C_6H_5NH_3^+$ and the anionic sodium dodecyl sulfate micelle has been concluded on the basis of a significant upfield shift of the proton signals of α- and β-CH_2 groups adjacent to the polar head of sodium dodecyl sulfate [16].

Since the initial state and the nature of the solubilized molecule and a group of atoms shielding the protons of α-CH_2 group play an important role,

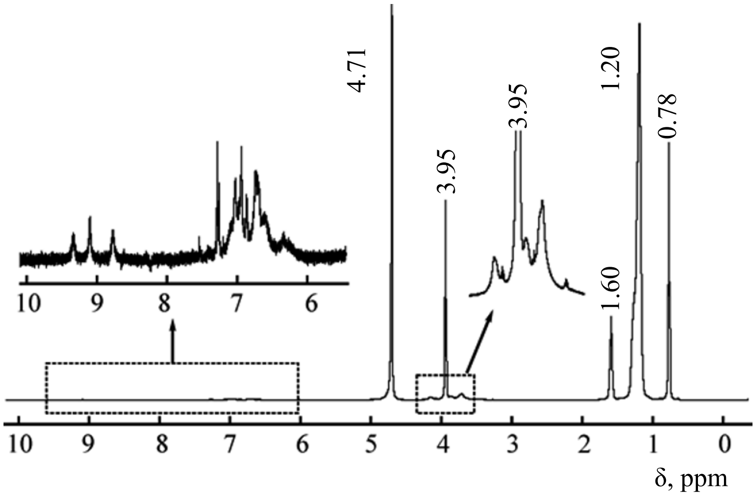

Fig. 5. ^{1}H NMR spectra of sodium dodecyl sulfate–**Id** in D_2O, [**Id**] = 0.0023 M.

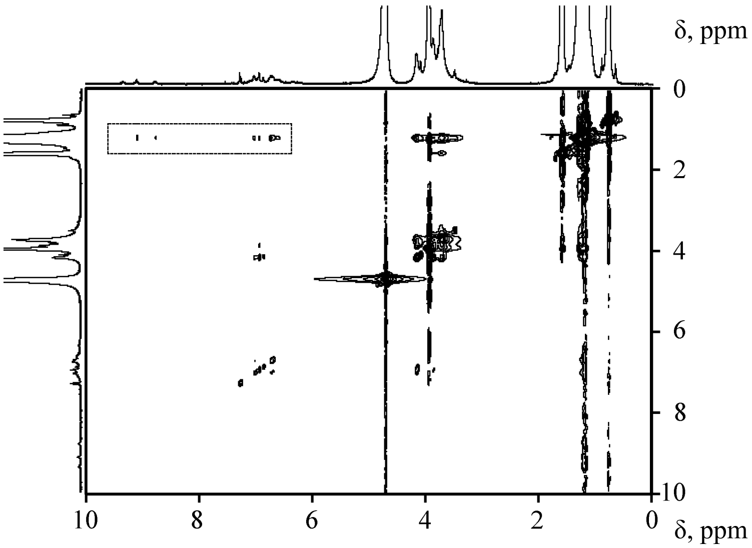

Fig. 6. NMR ^{1}H–^{1}H NOESY spectrum of sodium dodecyl sulfate–**Id** in D_2O, [**Id**] = 0.0023 M.

there is no clear trend in the behavior of chemical shift δ of the sodium dodecyl sulfate protons. Thus, in the presence of 5,10,15,20-tetrakis[4-(3-pyridiniumpropoxy)-phenyl]porphyrin tetrakis-bromide the observed shifts were in different directions: the signals of α-CH_2 protons were shifted downfield, while those of the protons of the other groups, upfield [17]. The ^{1}H signals of all groups of sodium dodecyl sulfate in the presence of $(p\text{-NH}_3^+)_1\cdot$ $TPPH_2$ [the protonated (*p*-aminophenyl)-20,15,20-triphenylporphyrin) [8] are shifted upfield, therewith, Δδ was higher for the protons of the hydrocarbon chain in both cases [8, 17]. These data were interpreted in favor of the inclusion of the macrocyclic compound in the sodium dodecyl sulfate micelle and its preferential localization in the hydrophobic region of the latter.

The data on the proton chemical shifts of all groups of sodium dodecyl sulfate in the presence of **Id**, two-dimensional ^{1}H–^{1}H NOESY experiment, and the EAS spectra of **Id** in micellar solutions of sodium dodecyl sulfate obtained in this paper are consistent with each other. It seems that they are more in line with the model of structural units of the micellar solution with binding phthalocyanine with the hydrophobic region of the micelle. Synergism of the effects such as *guest–host* (Na^+ ion chelation) for the phthalocyanine crown fragments, the electrostatic interaction of the polar OSO_3^- *head* with the complex-bound Na^+ ion, and the interactions of aromatic protons with protons of CH_2 groups of the hydrocarbon chain of sodium dodecyl sulfate can lead to the formation of such a species. The aforementioned aggregation of **Id** in the presence of cationic surfactants confirms the need for all these types of non-covalent interactions at the solubilization of phthalocyanine and the existence of **Id** in the form of micelle-bound monomer in solution of sodium dodecyl sulfate at the concentration of the latter close or slightly above the critical micelle concentration. On the contrary, a necessary condition for the **Id** location in the micelle shell, while maintaining the monomer state (according to absorp-tion spectra) of phthalocyanine in aqueous micellar sodium dodecyl sulfate solutions, is a stronger binding of phthalocyanine on the periphery of the charged micelles in the interfacial region compared with its inclination to aggregation in polar medium. The study of fluorescence quenching in the **Id**–sodium dodecyl sulfate system, the determination of hydrodynamic radius of the species of **Id**–sodium dodecyl sulfate micellar solution and others are likely to be useful in the discussion on the solubilization of octa-crown-containing phthalocyanine by anionic surfactant and the sites of binding phthalocyanine by the micelle.

Thus, using electronic spectroscopy in the UV and visible regions, and ^{1}H NMR spectroscopy, including two-dimensional ^{1}H–^{1}H correlation NOESY (Overhauser effect) we studied the behavior of **Id** in aqueous solutions of sodium dodecyl sulfate. We showed that in the microheterogeneous medium of aqueous sodium dodecyl sulfate at concentrations of the latter equal or higher than the CMC the **Id** is in monomeric form, while at the concentration of sodium dodecyl sulfate below CMC it is a dimer or in a more aggregated form. We found that the resonance of the protons of all groups of sodium dodecyl sulfate in the presence of **Id** are shifted upfield in comparison with the signals of the sodium dodecyl sulfate protons in the absence of the phthalocyanine. The change in the proton chemical shifts of methylene and methyl groups of the sodium dodecyl sulfate hydrocarbon chain is larger than the shifts of the protons of α- and β-CH_2 groups adjacent to its polar head. Results of two-dimensional ^1H–^1H NOESY experiment indicate that in the **Id**–sodium dodecyl sulfate system there is interaction of aromatic protons with the protons of methylene groups $(CH_2)_9$ of the sodium dodecyl sulfate hydrocarbon chain. This suggests preferential binding of **Id** by the micelle in the hydrophobic region of the latter.

EXPERIMENTAL

We used tetraoctylammonium bromide Oct_4NBr, sodium dodecyl sulfate $CH_3(CH_2)_{11}OSO_3Na$ 99% and sodium carboxymethylcellulose from Aldrich, KCl of analyticaly pure grade for electrochemistry. To prepare the solutions we used double-distilled water. Dichloromethane (for spectrophotometry, Aldrich) was distilled before use. Ethanol was dehydrated according to [18]. Solutions for NMR studies were prepared in D_2O (HOD content ~ 4.5%).

Spectrophotometric measurements were performed on a Specord M-40 instrument using quartz cells of 1, 2, and 10 mm or a thin layer (8×10^{-4} cm) between quartz plates.

^1H NMR spectra were recorded on a high-resolution Bruker AVANCE III instrument with an operating frequency of 500 MHz. The spectra were recorded at 22°C in conventional 5 mm tubes for high resolution NMR. Intermolecular interaction of closely spaced hydrogen atoms were revealed using two-dimensional ^1H–^1H correlation NOESY. The frequencies were calibrated relative to the signals of residual protons in D_2O (δ 4.71 ppm) in 0.32 M solution of sodium dodecyl sulfate without additives. To determine the relative change in the ^1H shifts from sample to sample, all spectra were recorded at the same magnetic field that was used for the registration of the spectrum of pure sodium dodecyl sulfate, minimizing the delay time. To confirm the data obtained was also used TMS as external reference (in a capillary).

Synthesis of magnesium 2,3,9,10,16,17,23,24-octa-[(4'-benzo-15-crown-5)oxy]phthalocyaninate (Id). A mixture of 200 mg (0.29 mmol) of 4,5-bis[4'-benzo-15-crown-5)oxy]1,2-dicyanobenzene [2] and 7 mg (0.29 mmol) of magnesium turnings in 20 ml of anhydrous *n*-butanol was refluxed for 48 h and then the solvent was removed in a vacuum. To the residue was added 20 ml of saturated solution of $(NH_4)_2SO_4$. A dark-green precipitate formed was filtered off, washed with water, and dried in air to a constant weight. Analytical sample was purified by column chromatography (SiO_2, eluent $CHCl_3$–CH_3OH, 20:1). Yield 0.16 g (80%).

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