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MOLECULAR AND SUPRAMOLECULAR STRUCTURES AT THE INTERFACES

Magnesium Octa[(4'-Benzo-15-Crown-5)-Oxy]Phthalocyaninate in Low-Molecular Hydrogels: Spectral Properties and Release under Stimulation

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Abstract—This work is dedicated to low-molecular hydrogels based on biodegradable sodium deoxycholate (SDC) and lysine hydrochloride (lys × HCl) with magnesium octa-[(4'-benzo-15-crown-5)-oxy]phthalocyaninate ($Mgcr_8Pc$) as the active component, namely, their synthesis, spectral properties of gel-solubilized $Mgcr_8Pc$, its release from the gel etc. Addition of $Mgcr_8Pc$ occurs both via the mixing of the components and via its diffusion from the aqueous solution into the phase of the formed SDC/lys × HCl gel. $Mgcr_8Pc$-containing hydrogels are thermoreversible. The state of $Mgcr_8Pc$ in the SDC/lys × HCl/NaCl gel at the room temperature and in the melt is studied using spectral methods. Gel melting releases $Mgcr_8Pc$ in the form of a micelle-bound monomer. The presence of the $Mgcr_8Pc$ monomer phase in the phthalocyanine-carrying supramolecular hydrogel causes fluorescent activity of the latter.

Keywords: crown–containing phthalocyanines, aggregation, monomerization, surfactants, supramolecular hydrogels, sodium deoxycholate, lysine hydrochloride, absorption and fluorescence spectroscopy

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INTRODUCTION

Owing to the possibility of their extensive application, including in delivery of pharmaceuticals, supramolecular gels are currently attracting much attention [1–11]. Their important features are high water content and the ability to retain the active component, as well as to transport and release it under certain exposure types (stimulation). For this purpose, variation of the pH and polarity of the medium, temperature mode, etc., can be used.

Gels based on small molecules are attractive due to the simplicity of this formation and the availability and biocompatibility of the initial compounds. Surfactants and amino acids are "construction" materials (e.g., [12–14]). Sodium deoxycholate (SDC) belongs to the family of bile acids [15] and is a natural surfactant and gelation agent. SDC is an anionic steroid micelle-forming compound and is characterized by planar "diphilicity" (Fig. 1), consisting in the presence of a convex hydrophobic and concave hydrophilic surfaces. This distinguishes it from traditional surfactants with their long alkyl "tails" and a small polar group. Monovalent cations play an important role in the formation of gels based on salts of bile acids and their organization [16].

Phthalocyanines (Pc) and supramolecular aggregates in their basis are used in molecular electronics devices and chemical sensors, as well as in medicine as photosensitizers. One of the possibilities of preventing the aggregation typical for Pc, including that in aqueous medium, is using surfactants, including natural ones, and developing an environment for Pc that is compatible with the biological medium. It has been shown (paper [17] and references therein) that crown-containing Pcs are solubilized in aqueous–micellar solutions of synthetic anionic sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS) with the formation of monomers and dimers at a surfactant concentration close to the critical concentration of micelle formation (CCM) and below it, respectively. Magnesium octa[(4'-benzo-15-crown-5)-oxy]phthalocyaninate ($Mgcr_8Pc$) is predominantly in the monomer state in solutions of sodium deoxycho-

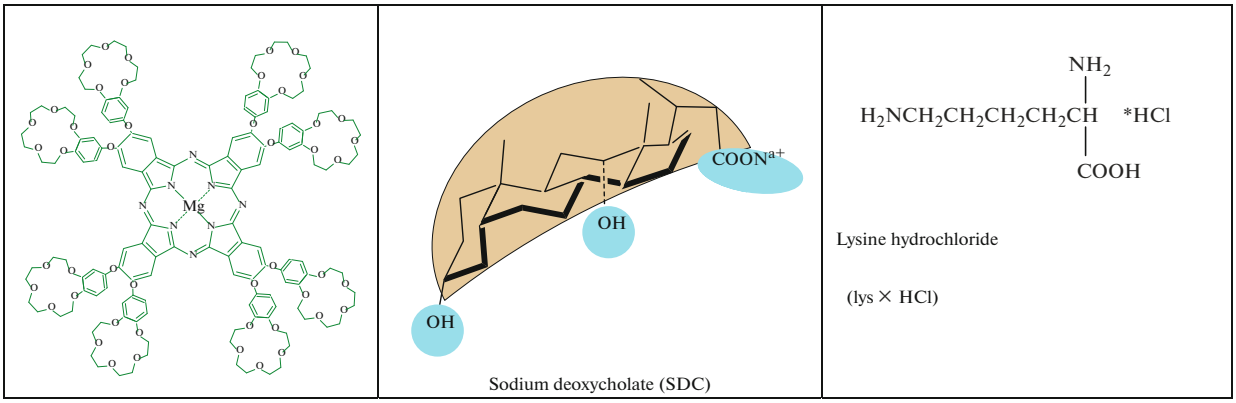

Fig. 1. Structural formulas of crown-containing phthalocyanines, sodium deoxycholate, and lysine hydrochloride.

late at an increase in ionic strength [18]. Solubilization of Mgcr$_8$Pc by micellar solutions of SDC allows considering the possibility of its incorporation into supramolecular gels.

This work is a continuation of studies of the behavior of crown-containing Pc in microheterogeneous media. It is dedicated to low-molecular hydrogels based on natural surfactants and amino acids with Pc as an active component, namely, their synthesis, spectral properties, release of Pc from the gel, etc. As far as we know, there are practically no studies of using Pcs as a component of low-molecular gels.

EXPERIMENTAL

Reagents. Synthesis of magnesium octa[(4'-benzo-15-crown-5)oxy]phthalocyaninate was carried out according to an earlier-published method [19]. SDS (Aldrich, 98%), SDC (Aldrich, 98%), lysine hydrochloride (99%) with no additional purification, and NaCl (for electrochemistry) were used in the work. All solutions were prepared using twice-distilled water.

The initial solution used was the aqueous Mgcr$_8$Pc solution with a known concentration. The reaction vessel was generally a 100-mm quartz cuvette transparent from all sides. Weighed samples of lys × HCl, SDC, and, if necessary, NaCl were successively added to the Mgcr$_8$Pc solution. Measurements were performed until a constant optical density value was reached. Stored samples were protected from exposure to light.

Formation of coatings. Immediately after recording EAS, 0.3 mL of each of the solutions of Mgcr$_8$Pc/SDC/lys × HCl and SDC/lys × HCl were applied onto a quartz glass surface with an area of 2 cm^2. The concentrations of Mgcr$_8$Pc, SDC, and lys × HCl in the solutions were 1.42×10^{-5}, 0.0264, and 0.124 M, respectively. The time of gel formation on quartz was ~15 min. The samples were dried at room temperature in a vessel closed off from light. Such a sample contained ~4.26×10^{-9} mol of Mgcr$_8$Pc.

Diffuse gel was obtained by application onto the formed gel surface of 0.2 mL of aqueous Mgcr$_8$Pc solution of known concentration. The overall volume was 2.3 mL. EAS registration was used for registration of Mgcr$_8$Pc diffusion and to case the boundary between the layers to disappear.

Fluorescence spectra of the background gel (SDC/lys × HCl), "direct" and "diffuse" Mgcr$_8$Pc/SDC/lys × HCl and Mgcr$_8$Pc/SDC/lys × HCl/NaCl gels were registered using a PerkinElmer LS55 spectrofluorimeter in 10-mm quartz cuvettes at room temperature in air. The concentrations of Mgcr$_8$Pc, SDC, lys × HCl, and NaCl were 8.65×10^{-6}, 0.02, 0.23, and 0.18 M, respectively. The optical width of the gap for excitation of fluorescence was 10 nm, and the detection angle was 90°. Excitation spectra of fluorescence were recorded at λ_{emit} = 683 and 704 nm; the emission spectra were recorded at λ_{exc} = 614 nm. The position and shape of the emission band are independent of the wavelength of the excitation light (614, 625, and 635 nm). The Raman band of the water is shifted by approximately 0.3 μm^{-1} into the long-wave region with respect to the excitation wavelength and is beyond the studied region [20]. Fluorescence for the background gel was absent in the case of sample excitation by light with the above wavelengths. EAS of gels remained unchanged.

Spectrophotometric measurements were carried out using a Specord M-40 spectrophotometer in solutions using 1-, 2-, and 10-mm quartz cuvettes or in a thin (0.002 cm) layer between quartz glasses at room temperature and on quartz glasses in the case of coatings. In a number of cases, absorption spectra were resolved into Gauss components using the Origin mathematical package.

IR spectra of individual sodium deoxycholate, lysine hydrochloride, and dried-gel samples on optical quartz and the gels themselves were measured using a

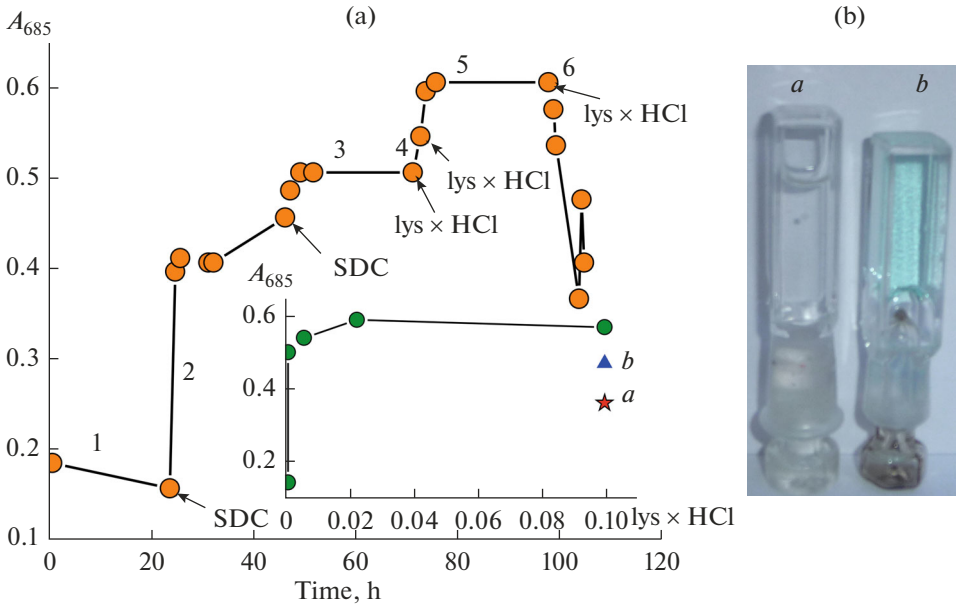

Fig. 2. (a) Variation of optical density (A_{685}) of the aqueous solution of $Mgcr_8Pc$ ([8.56×10^{-6} M]) in time in case of addition of lysine hydrochloride (region 1, [lys × HCl] = 1.25×10^{-3} M), sodium deoxycholate (regions 2 and 3, [SDC] = 9.9×10^{-3} and 21.7×10^{-3} M, respectively, [lys × HCl] = 1.25×10^{-3} M), lysine hydrochloride (regions 4, 5, and 6, [lys×HCl] = 6.2×10^{-3}, 22.7×10^{-3} and 100×10^{-3} M, respectively, [SDC] = 21.7×10^{-3} M). Inset: A_{685} *vs* [lys × HCl]; point *a*: optical density of hydrogel; point *b*: the same sample after heating to ~35°C. (b) Sample photographs: (*a*) SDC/lys × HCl viscous liquid and (b) SDC/lys × Cl/$Mgcr_8Pc$ hydrogel.

Perkin Elmer Spectrum 100 Fourier spectrometer (United States) with an UATR add-on in the range of 4000–675 cm^{-1} (Ge crystal).

RESULTS AND DISCUSSION

Formation of Phthalocyanine-Carrying Hydrogel Based on Sodium Deoxycholate and Lysine Hydrochloride

Lysine hydrochloride and sodium deoxycholate were chosen as the components of the supramolecular gel. Magnesium octa-[(4'-benzo-15-crown-5)-oxy]phthalocyaninate was selected as a model compound. Its electronic-absorption spectra (EASs) in the region of the Q-band are information carriers on the molecular state of phthalocyanine and its environment [17]. The appearance of a wide band in the range of 630–750 nm in the EAS indicates an aggregated state of $Mgcr_8Pc$ in water. At the same time, there are no bands in the EAS that allow identifying the solid Pc phase [21].

Figure 2 shows the dependence of optical density of the $Mgcr_8Pc$ aqueous solution on time when lys × HCl and SDC are successively added. In case of a low lys × HCl concentration, the EAS in region 1 is practically the same as the spectrum of the aqueous $Mgcr_8Pc$ solution. When SDC is added into the $Mgcr_8Pc$/lys × HCl system, just as in case of pure SDC [18], the optical density of the solution in the region of the Q-band increases (regions 2 and 3). Here, Pc aggregation is preserved (Fig. 3). The further addition of lys × HCl occurred already with SDC in the solution ([SDC] ≫ CCM_1). One can see that, under these conditions, an increase in the concentration of lys × HCl (Fig. 2) results in a certain increase in the optical density (regions 4 and 5) with the absorption spectrum of $Mgcr_8Pc$ close to the spectra of phthalocyanines in regions 2 and 3. EASs are characterized by a hypsochromic shift of the Q-band from 689 to 685 nm.

At the concentrations of lysine hydrochloride comparable with the NaCl concentration, i.e., about 0.1 M [18], a decrease in the optical density of the solution at 685 nm (Fig. 2a, inset) accompanied by gel formation was observed. The formed dense gel preserves the shape and position in an overturned vessel, which is a simple test of its formation (Fig. 2b). Under mechanical exposure (prolonged vigorous shaking), the gel manifests the properties of thixotropic liquid.

When EASs were presented in the form of Gauss components, it appeared that the spectra of $Mgcr_8Pc$ in hydrogel and in the aqueous solution of SDC/lys × HCl were similar in number, position, and shape of components. There are components in the EASs that, according to their values of λ_{max}, can be considered as an indication of appearance of a certain amount of the $Mgcr_8Pc$ monomer formed as a result of Pc solubilization in a microheterogeneous medium by micelles of SDC or SDC/lys × HCl. Comparison of the EAS of the micellar solution of $Mgcr_8Pc$/sodium dodecylsulfate (Fig. 3, inset) with the EAS of the microheteroge-

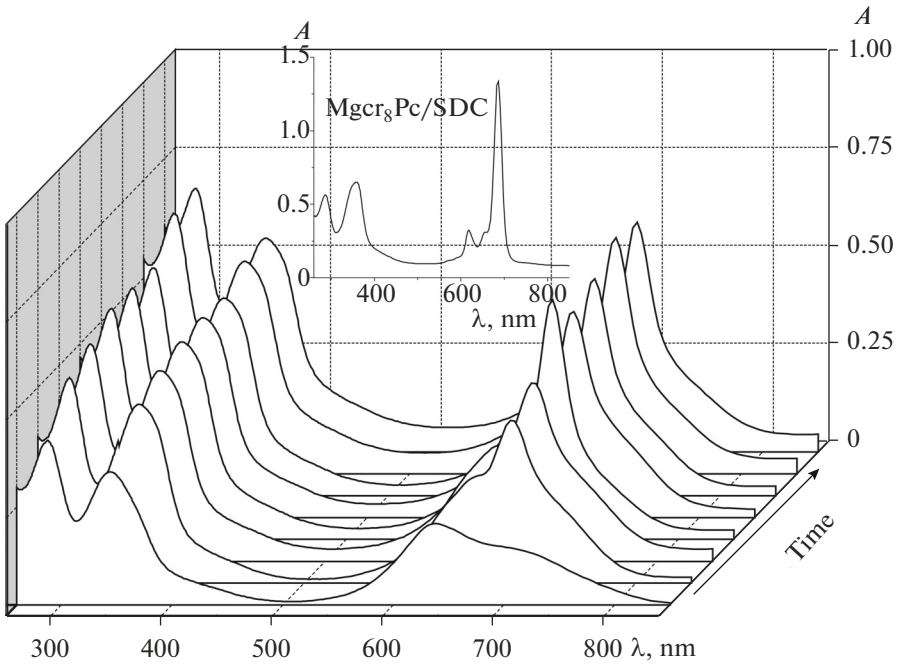

Fig. 3. Variation of EASs in the course of the maturing of the $Mgcr_8Pc$/SDC/lys × HCl gel. The spectrum of the $Mgcr_8Pc$/SDC micellar solution (inset) is shown for comparison.

neous system of $Mgcr_8Pc$/SDC/lys × HCl (Figs. 2, 3) provides a clear idea as to the difference in the state of $Mgcr_8Pc$, namely, as to existence of Pc in the monomeric and noticeably aggregated forms, respectively. The addition of NaCl to gel did not result, as opposed to in the case of paper [13], in its decomposition, but the concentration of the monomeric state of $Mgcr_8Pc$ increased. Nevertheless, both gels ($Mgcr_8Pc$/SDC/lys × HCl and $Mgcr_8Pc$/SDC/lys × HCl/NaCl) at [lys × HCl] > [SDC] are characterized by a considerably higher aggregation degree of Pc (Figs. 2 and 3) as compared to the $Mgcr_8Pc$/SDC/NaCl solution, in which Pc was predominantly in a monomeric state [18].

Ways to Form Pc-Containing Gels

$Mgcr_8Pc$-containing gel is formed as a result of mixing the process components ("direct" gel (see above)) or Pc diffusion from the aqueous solution into gel formed from SDC and lys × HCl at a ratio of 1 : 12 ("diffuse gel"). Photographs of the sample denoted by numbers 1 and 2 (Fig. 4) shows a dense gel of SDC and lys × HCl at a ratio of 1 : 12, onto which the aqueous $Mgcr_8Pc$ solution is placed later (sample 3). The sample height (sum of heights of the gel layer and layer of the aqueous Pc solution) remains practically unchanged in the course of diffusion of $Mgcr_8Pc$ into the gel ([$Mgcr_8Pc$] ⋘ [SDC] or [lys × HCl]). The arrow points to the direction of movement of Pc. Simultaneously, a sample of "direct" gel of $Mgcr_8Pc$/SDC/lys × HCl was also prepared.

The EASs (Fig. 4b) indicate both diffusion of Pc (increase in the concentration of $Mgcr_8Pc$ in the gel phase) and to its predominantly aggregated state. Expansion of the spectral line by Gauss functions allows, just as in the case of "direct" gel, suggesting that a small concentration of the monomeric form of Pc is present (Fig. 5). The EASs of "direct" and "diffuse" gels at large times differ negligibly, which can be considered evidence of equilibrium being achieved in both cases.

Effect of NaCl

At room temperature, the absorption spectrum of $Mgcr_8Pc$ in the gel remains unchanged for a long time. The heating of the $Mgcr_8Pc$/SDC/lys × HCl and $Mgcr_8Pc$/SDC/lys × HCl/NaCl gels in the range of 45–55°C is accompanied by their melting. The temperature range depends on the ratio of components used for obtaining the gel. The change in the phase state of the $Mgcr_8Pc$/SDC/lys × HCl/NaCl system is accompanied by significant changes in the EAS of gel–solubilized $Mgcr_8Pc$, namely, an increase in optical density in the region of the Q-band and variation of its shape as compared with the gel (Fig. 6a, inset *b*).

Analysis of the absorption spectra of $Mgcr_8Pc$ in the molten $Mgcr_8Pc$/SDC/lys × HCl/NaCl gel and in the CH_2Cl_2 solution (Fig. 7a) with involvement of the first-order derivatives (Fig. 7b) allows stating their proximity. Qualitatively, EAS reflecting the state of $Mgcr_8Pc$ in the molten gel can be presented as a sum

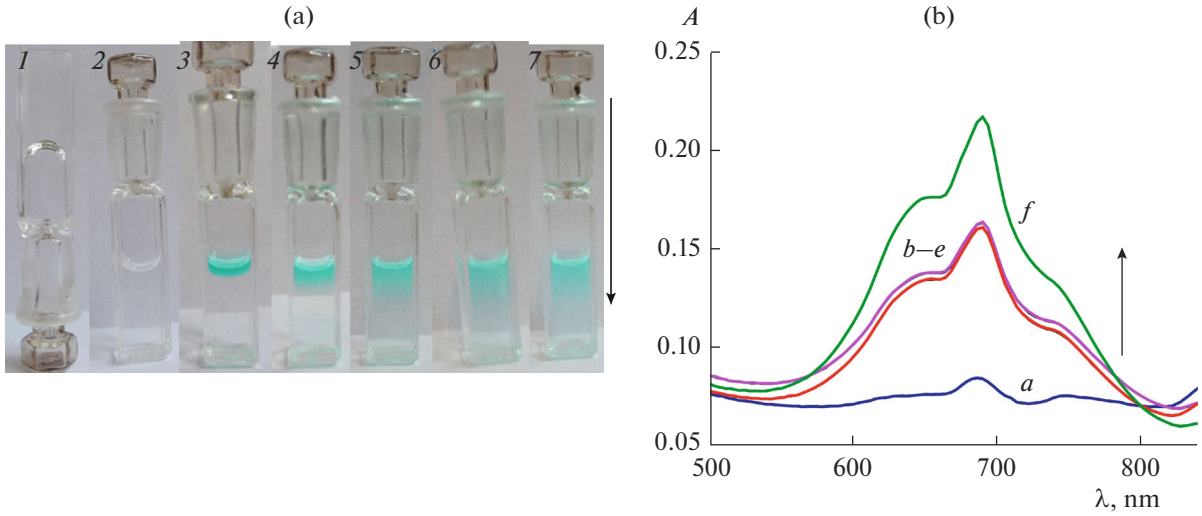

Fig. 4. Photographs and absorption spectra of gels. (a) Diffusion of $Mgcr_8Pc$ from the aqueous solution (the upper blue-green layer) into the SDC/lys × HCl/H_2O gel (numbers *1* and *2* indicate the SDC/lys × HCl/H_2O sample, while numbers *3*–*7* indicate the sample with a Pc-containing layer in the time range of 5 days. (b) Variation of EAS of the gel at an increase in the concentration of $Mgcr_8Pc$. The time range between the spectra (*a*–*g*) is 5 days, EASs (*b*–*e*) were recorded in 1 day. [$Mgcr_8Pc$] = 8.28 × 10^{-6} M, [SDC] = 0.021 M, [lys × HCl] = 0.25 M.

of four components taking into account the possible presence of high-order aggregates (Fig. 7c).

When $Mgcr_8Pc$/SDC/lys × HCl/NaCl is cooled, the optical density decreases as the gel "matures" (Fig. 6a, inset *a*). $Mgcr_8Pc$-containing gels are thermally reversible, and the heating–cooling stages can be repeated many times (Fig. 6b, inset). Photodecolorization of gel-solubilized $Mgcr_8Pc$ is slow compared to in the case of micellar solutions [22], in which it is in the form of a monomer, which is related to fast monomer–aggregates–monomer transitions at a change in the phase state of the system and protective effect of the gel. The occurrence of photodegradation Pc in aqueous solutions without any change in the shape of the Q-band and appearance of new bands has been shown, e.g., for Pc with eight methylphosphonate groups [23].

Studies of Gels

A. Strength of the $Mgcr_8Pc$/SDC/lys × HCl/NaCl/H_2O gel

As has already been shown, preservation of the position in the inverted vessel is a test of gel formation. Gel loading can be considered as a test of its mechanical strength. Thus, 0.097 g of quartz plates of irregular shape with the size of 1.0–1.5 mm were applied onto the surface of the $Mgcr_8Pc$/SDC/lys × HCl/NaCl/H_2O gel (S = 1.0 cm^2) (Fig. 8, no. 1), which corresponds to the set pressure of ~10 Pa. The positions of plates, same as the state of the gel remained unchanged for 2 h (Fig. 8, no. 2). When the gel melts, the plates move down.

B. IR spectra of $Mgcr_8Pc$/SDC/lys × HCl gels

Figure 9 shows EASs of samples: dry gel on quartz prepared for measurement of IR spectra. The absorption spectra of $Mgcr_8Pc$ in gel and in gel dried in air are different on the region of the Q-band (Figs. 5, 9). The EAS of the dry gel also differs, e.g., from the spectrum of MgPc(H_2O) in the film [21].

IR spectra recorded in the ATR mode for the components of the $Mgcr_8Pc$/SDC/lys × HCl system,

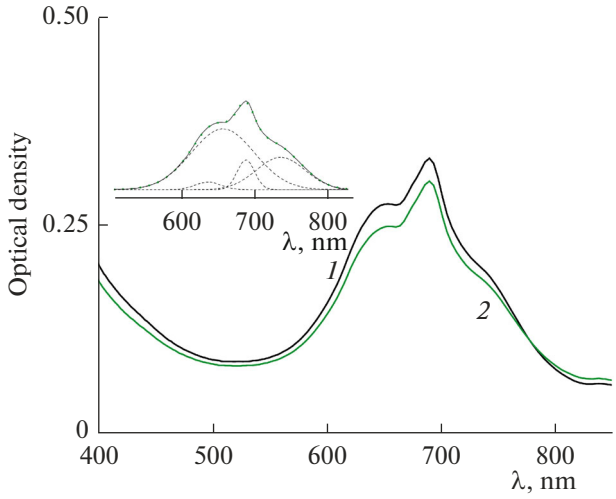

Fig. 5. EASs of (*1*) the "direct" and (*2*) "diffuse" hydrogels of $Mgcr_8Pc$/SDC/lys × HCl after prolonged storage. The spectra were recorded before addition of the NaCl sample. Inset: Expansion of spectrum *2* by Gauss functions (R^2 = 0.999).

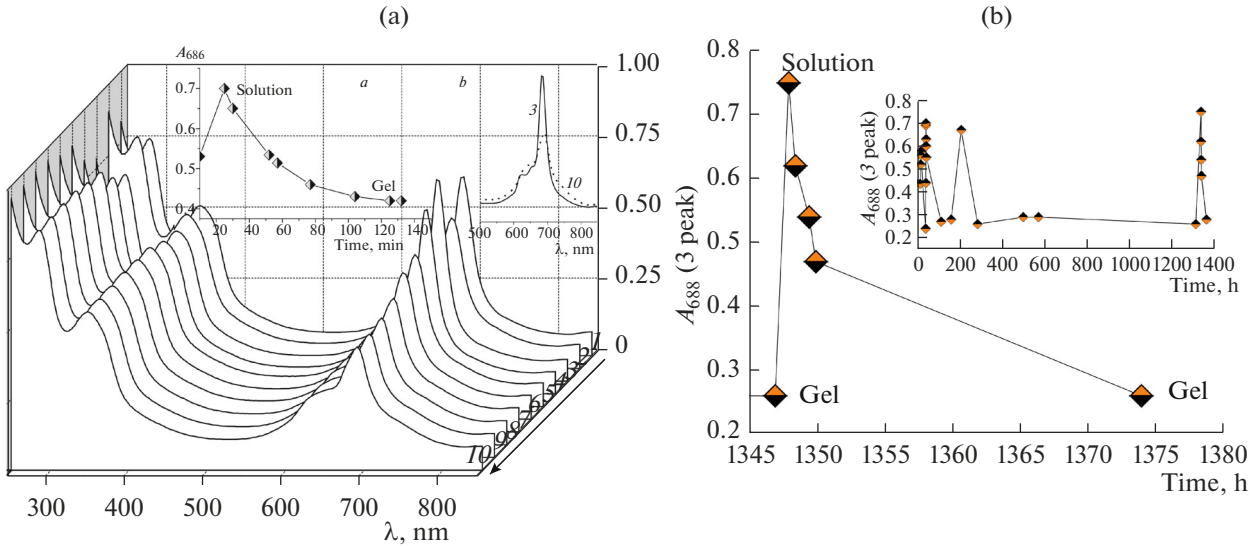

Fig. 6. (a) Changes in EAS of "direct" gel. Inset (*a*): Formation of a dense $Mgcr_8Pc/SDC/lys \times HCl/NaCl/H_2O$ hydrogel from the melt (55°C) in the course of the cooling of the latter to room temperature (18°C). Inset (*b*): Absorption spectra of the solution (melt) of the hydrogel (spectrum *3*) and dense hydrogel (spectrum *10*) of $Mgcr_8Pc/SDC/lys \times HCl/NaCl/H_2O$. (b) Optical density of peak *3* (A_{688}) from the expansion of the spectral curve for the $Mgcr_8Pc/SDC/lys \times HCl/H_2O$ gel by Gauss functions as a time function: gel (20°C) → solution (~50°C) → gel (20°C). The repeated graph part is shown. Inset: graph A_{688} *vs* time.

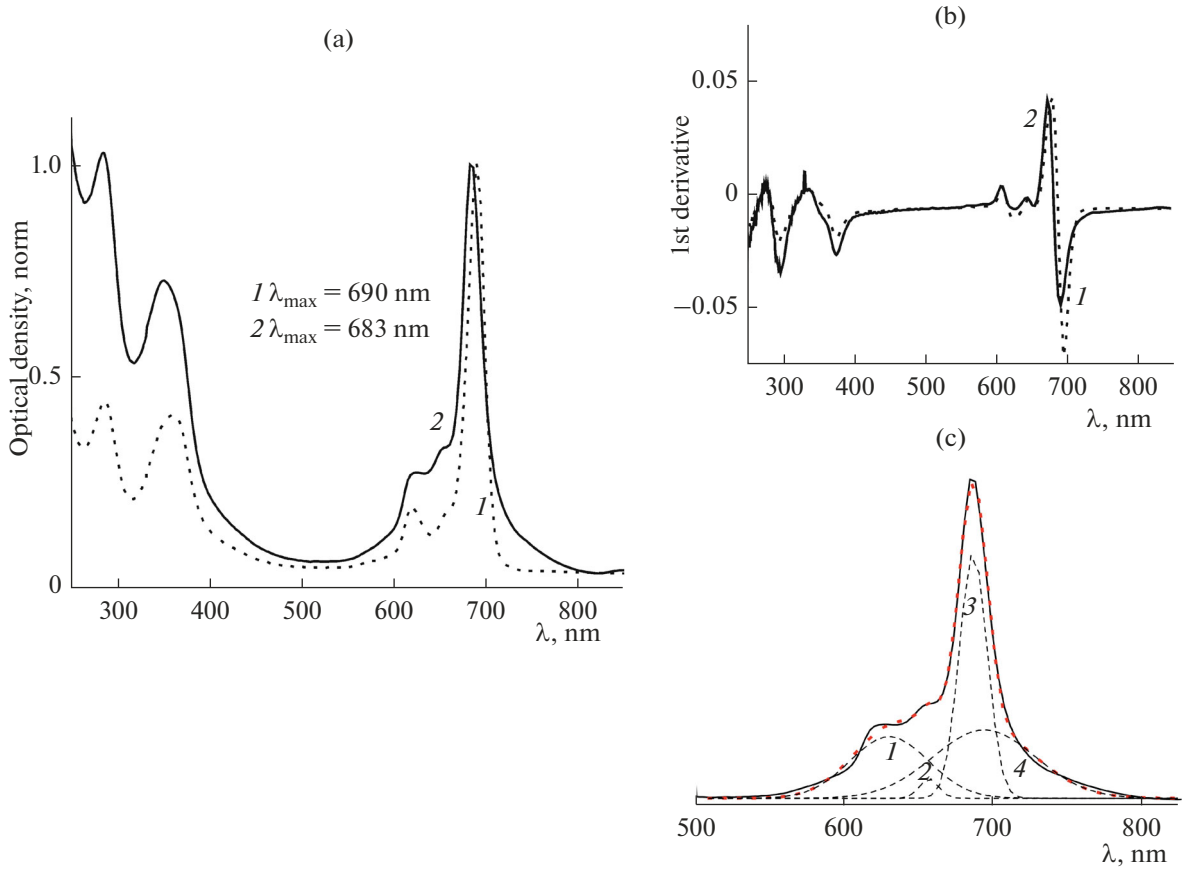

Fig. 7. (a) Absorption spectra for (*1*) $Mgcr_8Pc$ in dichloromethane and (*2*) $Mgcr_8Pc$ in molten $Mgcr_8Pc/SDC/lys \times HCl/NaCl$ gel. (b) First derivatives of EAS (*1*) and (*2*). (c) Qualitative representation of EAS of the $Mgcr_8Pc/SDC/lys \times HCl/NaCl$ gel in the form of four components in expansion by Gauss functions ($R^2 = 0.997$).

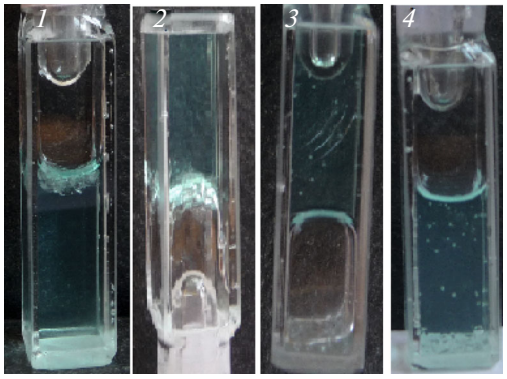

Fig. 8. Photographs of samples of $Mgcr_8Pc/SDC/lys \times HCl/NaCl/H_2O$ with added quartz (*1*, *2*) before and (*3*, *4*) after gel melting, respectively. Photograph *3* is inverted for illustrative purposes.

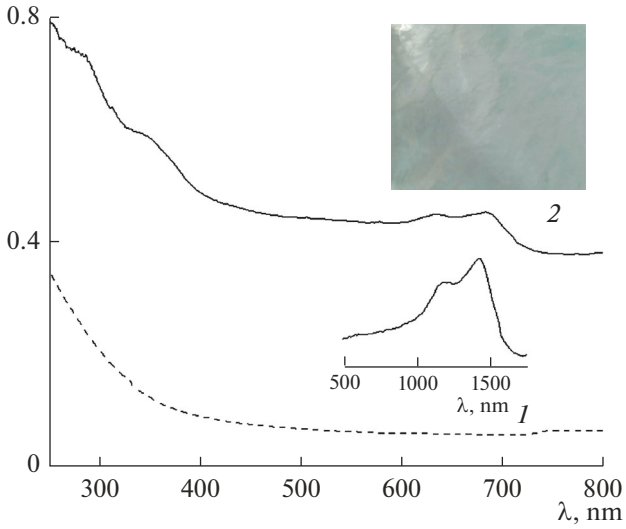

Fig. 9. EASs of coatings dried in air: from (*1*) viscous solution of SDC/lys × HCl and (*2*) hydrogel of $Mgcr_8Pc/SDC/lys \times HCl$ on quartz. Insets: coating fragments and the region of the Q-band.

namely, powders of $Mgcr_8Pc$, SDC, and lys × HCl, as well also the gel dried in air, are shown in Fig. 10. The lys × HCl spectrum is characteristic for the dehydrated form [24] and the spectrum of SDC is typical for the crystalline state. All bands in the IR spectrum of the dry gel are broadened as compared to individual compounds. The IR spectra recorded for different coating points differ in the values of the intensities of bands, which is related to the appearance of nonuniformities when the gel dries. Relatively intense bands for all gel components are in the region of 1750–850 cm^{-1}. Let us note that the characteristic bands of $Mgcr_8Pc$ in the IR spectrum of the dried gel are practically invisible owing to the large excess of gel-forming compounds and lys × HCl, particularly over Pc (spectrum *4*). Therefore, the EASs are evidence of the presence of Pc in the coating. Vibrations of $\nu(COO^-)_{as}$ at 1562 cm^{-1} for SDC overlap $\nu_{as}(NH_3^+)$ of lysine hydrochloride [24] (Fig. 10a). The shoulder at 1670 cm^{-1} in spectrum *4* (Fig. 10a) may indicate a weak hydrogen bond between the carboxylate anion of SDC (or lys × HCl) and protons of ammonium cation of lys × HCl or residual water molecules in the solid state. According to the IR spectra in paper [24], both amino groups of *l*-lys × HCl (both hydrated and anhydrous) are in the protonated state. Nevertheless, the IR spectrum of the dried gel, in our opinions shows no clear signs of the presence of $\nu(COO^-)$ as the vibration of carboxyl in deoxycholic acid (~1700 cm^{-1}) [25], though this would point to formation of a network of hydrogen bonds in the gel. This, in addition to other causes (destruction of the gel microstructure) can probably explain the difference between electronic absorption spectra of $Mgcr_8Pc$ in the gel and in a solid sample. A weakly structured wide band in the region of 3500–2500 cm^{-1} (spectrum *4*) alongside with ν_{as} and ν_s of valence vibrations of the C–H bonds in methylene groups of SDC and lys × HCl includes the vibration frequencies of the N–H bonds on the ammonium cation of lys × HCl [24] (Fig. 11b) and also Raman bands.

IR spectra of the supramolecular $Mgcr_8Pc/SDC/lys \times HCl$ system (lys × HCl/SDC ~ 1) were also recorded in the water-evaporation mode. For this, a gel microdrop was placed onto the Ge crystal. While the first spectrum in Fig. 11a shows only water, its evaporation resulted in appearance of bands of the deoxycholate anion. The position of frequencies of valence vibrations of C–H bonds in sodium deoxycholate in the gel spectrum remained practically unchanged as compared to their position in the SDC spectrum. The vibration frequency corresponding to carboxylate in SDC is shifted toward low values (as compared to a crystalline SDC sample) (Figs. 11a, 11b), which can be considered as involvement of SDC in the supramolecular gel organization [26].

C. Fluorescence in "Direct" and "Diffuse" $Mgcr_8Pc/SDC/lys \times HCl/NaCl/H_2O$ Gels

Fluorescence spectra reflect the content of the monomer form of Pc, while absorption spectra indicate the presence of monomers and aggregates of different composition that are characterized by different, often unknown, extinction coefficients. The $Mgcr_8Pc/SDC/lys \times HCl/NaCl/H_2O$ systems ("direct" and "diffuse" gel) are characterized by a low concentration of the presumably monomeric form of $Mgcr_8Pc$ (Fig. 5). Moreover, they are not only microheterogeneous systems, but also gels, which can result in underestimated values of fluorescence intensity due to light scattering [27]. However, the presence of fluo-

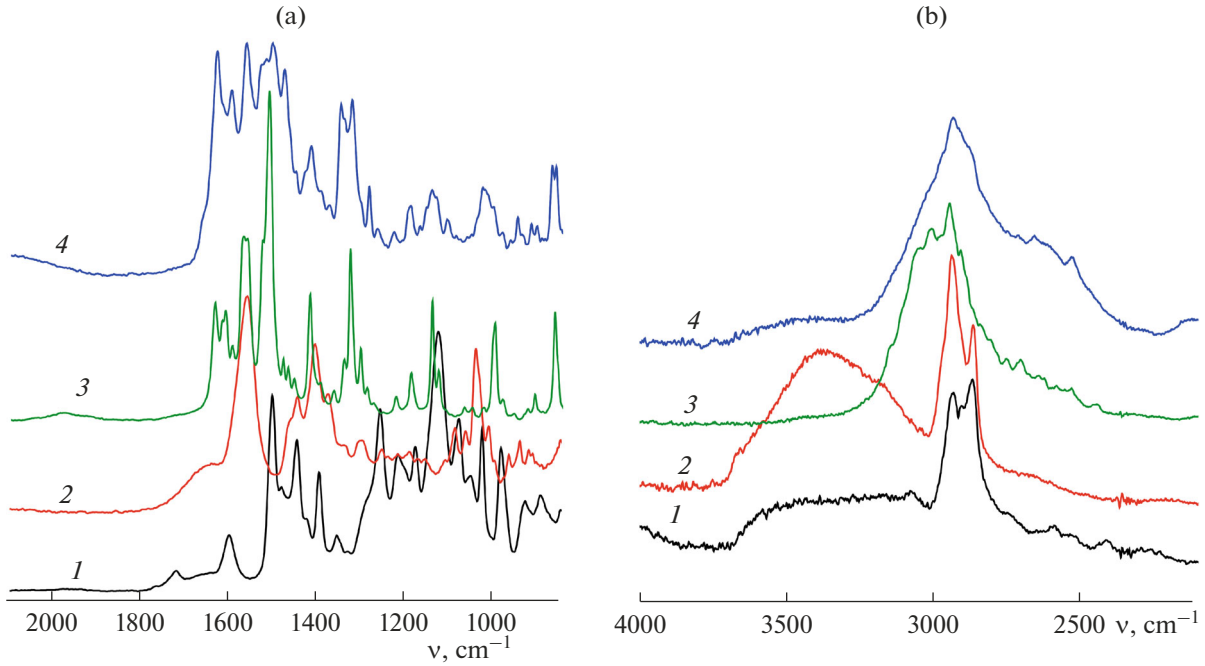

Fig. 10. IR spectra of (*1*) $Mgcr_8Pc$, (*2*) SDC, (*3*) lys × HCl, and (*4*) the $Mgcr_8Pc$/SDC/lys × HCl (lys × HCl/SDC ~ 5) gel on quartz dried in air.

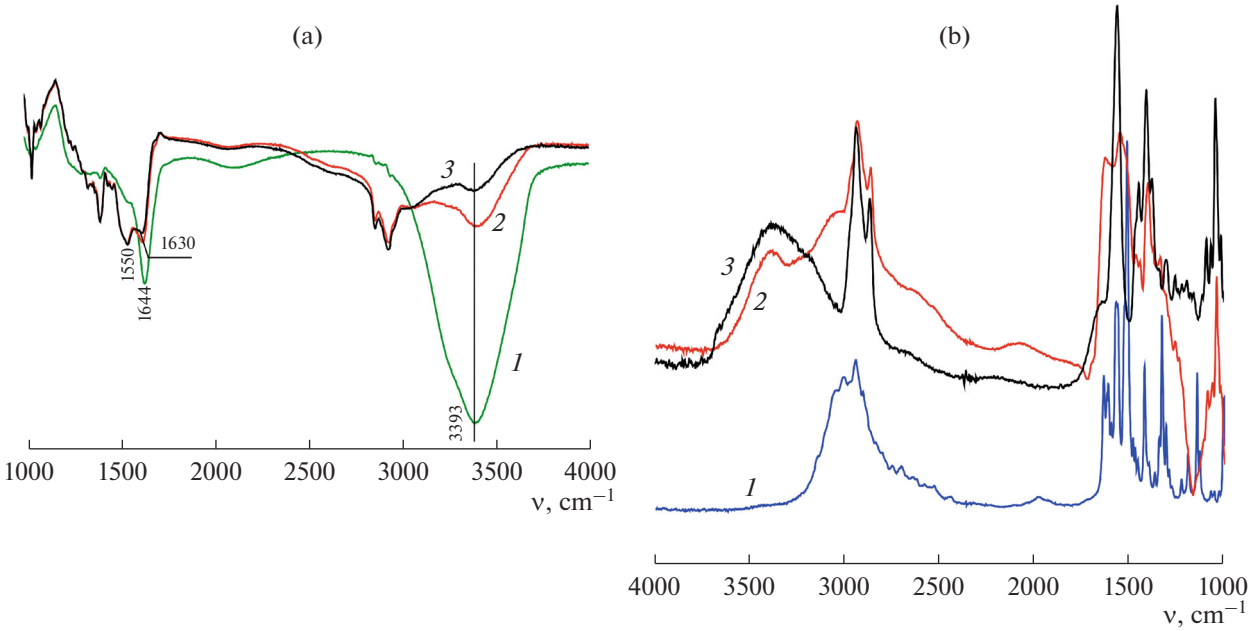

Fig. 11. (a) Variation of IR spectra of the $Mgcr_8Pc$/SDC/lys × HCl gel in the course of water evaporation (*1–3*). (b) *IR* spectra of (*1*) lysine hydrochloride; (*2*) the $Mgcr_8Pc$/SDC/l lys × HCl gel, where lys × HCl/SDDC ~ 1; and (*3*) sodium deoxycholate.

rescence that points to the formation of fluorescence-active supramolecular hydrogel based on low-molecular compounds: a surfactant and an amino acid with a $Mgcr_8Pc$ monomer as an active component.

As follows from Fig. 12a, the position and shape of the emission band of $Mgcr_8Pc$ in the sample of the $Mgcr_8Pc$/SDC/lys × HCl/NaCl diffuse gel is practically independent of the wavelength of the exciting

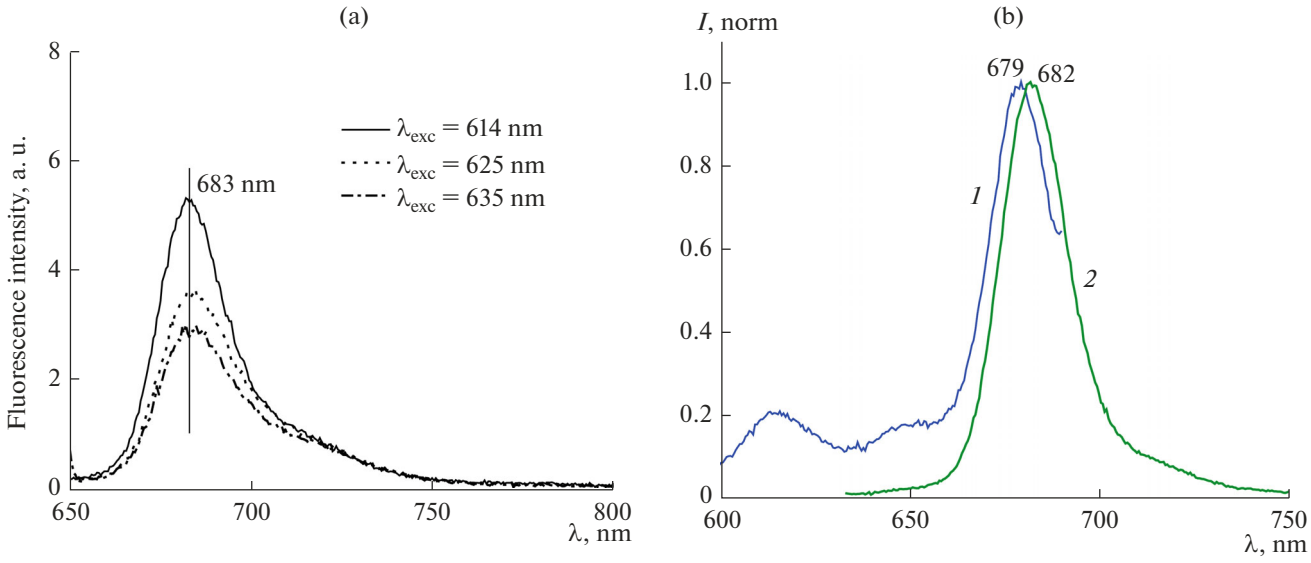

Fig. 12. (a) Effect of the wavelength of the excitation light on the position of the emission band of $Mgcr_8Pc$ in the "diffuse" gel. (b) Normalized spectra of excitation of fluorescence and emission of the $Mgcr_8Pc$/SDC/lys × HCl hydrogel at (*1*) $\lambda_{emit.} = 704$ and (*2*) $\lambda_{exc.} = 614$ nm, respectively.

light (614, 625, and 635 nm). All wavelengths are in the range of the satellite line of the longwave Q-band and in direct vicinity of its maximum. For the further work, $\lambda_{exc.} = 614$ nm was chosen as the one with the highest energy. Figure 12B shows fluorescence excitation and emission spectra of $Mgcr_8Pc$. One can see that the excitation spectrum repeats the shape of the absorption spectrum of the monomeric form of Pc (Fig. 6b, inset *b*). The "direct" gel sample behaved similarly to the "diffuse" gel sample, namely, it was fluorescence-active, but the intensity of fluorescence was not high.

According to EASs, $Mgcr_8Pc$ is in the solution (melt) of the $Mgcr_8Pc$/SDC/lys × HCl/NaCl gel predominantly in the monomeric state (Fig. 6a, inset *b*; Fig. 7). This was confirmed in measurement of the sample luminescence: namely, a change in the phase state of the $Mgcr_8Pc$/SDC/lys × HCl/NaCl system results in enhancement of intensity of fluorescence by approximately an order of magnitude (Fig. 13), which indicates destruction of the hydrogel microstructure in the course of the melting and release of $Mgcr_8Pc$ in the very form of a micelle-bound monomer (SDC–Pc). Thus, $Mgcr_8Pc$ in the gel melt is in the state close to its state in the $Mgcr_8Pc$/SDC/NaCl solution [18]. The emission band of $Mgcr_8Pc$ in the gel melt is shifted bathochromically by 3 nm with respect to its position in a dense gel. Fluorescence was absent for aggregated $Mgcr_8Pc$ samples in the pure aqueous solution or in the presence of lys × HCl.

Supramolecular organization of the gel is based on amphiphilic properties characteristic for SDC. A molecule of sodium deoxycholate is a rigid, almost planar steroid skeleton that has hydroxyl groups on the hydrophilic surface and methyl groups on the hydrophobic surface, and also a carboxyl group bound via a short alkyl spacer. This distinguishes SDC from conventional surfactants with their long mobile alkyl "chains" and a small polar group (Fig. 14). Primary SDC aggregates (micelles) are formed owing to hydrophobic interactions and are characterized by a small aggregation number [28, 29]. They are bound via their hydrophobic surfaces, while the hydrophilic surface is turned to the aqueous phase (Figs. 14b, 14c) [30]. The binding of two deoxycholate ions via hydrogen bonds

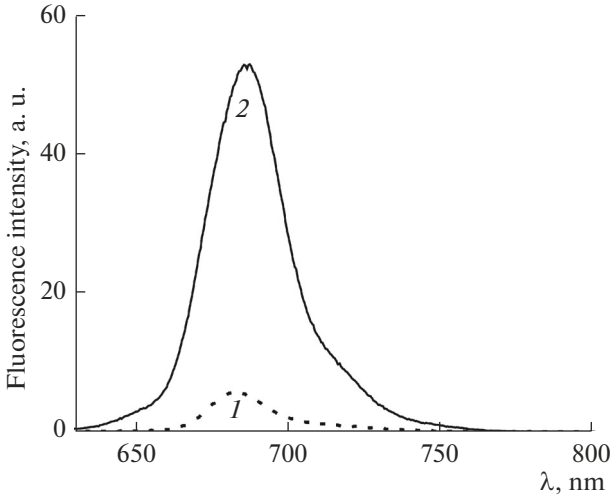

Fig. 13. Emission spectra of (*1*) the $Mgcr_8Pc$/SDC/lys × HCl/NaCl gel and (*2*) its melt, $\lambda_{exc} = 614$ nm.

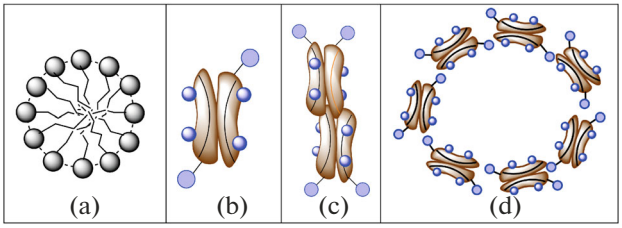

Fig. 14. Schematic image of (a) a sodium dodecylsulfate micelle and (b) aggregates (micelles) of sodium deoxycholate: (b, c) primary and (d, spiral) secondary.

is improbable at the surfactant concentrations used in the work ([SDC] < 30×10^{-3} M [31]).

$Mgcr_8Pc$ in the gel at a low SDC concentration in the presence of lys × HCl is in the aggregated state. The presence of a $-NH_3^+$ hydrophilic polar group in lys × HCl in the absence of a hydrophobic one produces practically no effect on the aggregation degree of the crown-containing Pc in aqueous solution and apparently favors formation and strengthening of the gel with participation of SDC and Pc, similarly to monovalent cations [16]. Under certain conditions, amino acids, on the contrary, promote destruction of the gel [7, 13].

The behavior of lys × HCl confirms that the Na^+ ion plays a role in the formation of micelle-bound Pc monomers, in particular, $Mgcr_8Pc$, in the course of solubilization of crown-containing Pcs by anionic surfactants in the aqueous medium. Addition of sodium chloride into the $Mgcr_8Pc$/SDC/lys × HCl gel results in an increase in the concentration of the $Mgcr_8Pc$ monomer, similar to as in paper [18]. It is known that an increase in the concentration of NaCl results in a decrease in the critical concentration of micelle formation of SDC. In 0.1 M aqueous solution of sodium chloride, it is 1.18×10^{-3} M [32]. Encapsulation of Na^+ ions in the case of crown-containing Pcs is shown using the ^1H NMR method in the example of interaction between Pcs and the annealed crown fragment and Na^+ in the organic solvent [33].

At the same time, only thermal stimulation of the gel favored separation of $Mgcr_8Pc$, predominantly in the form of a micelle-bound monomer. Variation of the phase state of the system at an increase in the temperature results in destruction of a 3D network formed in the gel as a result of weak, but numerous interactions, including hydrogen bonds in an aqueous medium. After thermal stimulation of the gel, a combination of complexation of the Na^+ ion with the crown ether cavity (the substituent fragment in the macrocycle), electrostatic and hydrophobic interactions results in release of $Mgcr_8Pc$ as a micelle-bound monomer similarly to the $Mgcr_8Pc$/SDS/NaCl system. At the stage of gel cooling and formation of new bonds between molecules, including hydrogen bonds, an environment appears in which phthalocyanine molecules predominantly aggregate, and only a few remain in the monomeric form, which affects the intensity of fluorescence, is recreated. Predominant data obtained using the IR-spectroscopy technique for the $Mgcr_8Pc$/SDC/lys × HCl gel and samples of gel dried in air agree with these notions.

CONCLUSION

Thus, the formation of low-molecular gels based on natural compounds (sodium deoxycholate and lysine hydrochloride) with inclusion of magnesium octa-[(4'-benzo-15-crown-5)-oxy]phthalocyaninate as an active component is shown. Absorption spectra for the $Mgcr_8Pc$/SDC/lys × HCl/NaCl/H_2O gel and molten gel demonstrate variation of the state of $Mgcr_8Pc$ and an increase in the concentration of its monomer at a change in the phase composition of the system. The data of absorption spectroscopy on the presence of the predominantly monomeric state of $Mgcr_8Pc$ are confirmed by the results of fluorescence spectroscopy. The formation of fluorescence–active supramolecular gels with inclusion of magnesium octa-[(4'-benzo-15-crown-5)-oxy]phthalocyaninate agrees with the presumable formation of a 3D network of hydrogen bonds.

Studying the structure of low-molecular gels with participation of crown-containing phthalocyanines as an active component and possibility of including other Pcs is the subject of the further research.

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