

## Supramolecular Organization of Magnesium Octa[(4'–benzo–15–crown–5)oxy]phthalocyaninate in Aqueous Solutions of Polyelectrolytes and Surfactants: Analysis by Spectral Methods

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*The behavior of magnesium octa[(4'-benzo-15-crown-5)-oxy]phthalocyaninate ( $Mgcr_8Pc$ ) in aqueous solutions of polyelectrolytes as well as their mixtures with anionic surfactants such as sodium dodecyl sulfate and biocompatible sodium deoxycholate has been studied. A synergistic effect of sodium deoxycholate and sodium polystyrene sulfonate promotes  $Mgcr_8Pc$  monomerization in the aqueous environment. For the first time, it was shown that fluorescent hydrogel was formed in the  $Mgcr_8Pc$ /sodium deoxycholate/lysine hydrochloride system. In all cases, the existence of  $Mgcr_8Pc$  as a micelle-bound monomer has been confirmed by the increase of the emission intensity, since aggregates and H-dimers do not fluoresce.*

**Keywords:** Phthalocyanine, absorption spectra, fluorescence, monomerization, anionic surfactants, sodium polystyrene sulfonate, sodium deoxycholate, hydrogel.

## Супрамолекулярная организация окта[(4'–бензо–15–краун–5)окси]фталоцианината магния в водных растворах полиэлектролитов и поверхностно–активных веществ: анализ спектральными методами

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*В водных растворах полиэлектролитов, а также их смесях с анионными поверхностно-активными веществами, такими как додецилсульфат натрия и биосовместимый дезоксихолат натрия изучено поведение окта[(4'-бензо-15-краун-5)-окси]фталоцианината магния ( $Mgcr_8Pc$ ). Синергетическое действие дезоксхолата натрия и полистиролсульфоната натрия способствует мономеризации  $Mgcr_8Pc$  в водной среде. Впервые показано, что флуоресцентно-активный гидрогель образуется в системе  $Mgcr_8Pc$ /дезоксихолат натрия/лизин-гидрохлорид. Каждый компонент участвует, по-видимому, в образовании водородных связей и в результате вносит свой вклад в формирование устойчивого геля. Во всех случаях существование  $Mgcr_8Pc$  в виде мицелло-*

связанного мономера подтверждено ростом интенсивности люминесценции, поскольку агрегаты и *H*-димеры фталоцианина не являются фотоактивными.

**Ключевые слова:** Фталоцианин, спектры поглощения, флуоресценция, мономеризация, полистиролсульфонат натрия, дезоксихолат натрия, гидрогель.

## Introduction

Supramolecular chemistry is one of the youngest fields of chemistry. It is a field in which molecules are often close in structure and functions to biological ones and participate in processes of self-assembling to form objects of supramolecular chemistry (supramolecular ensembles) due to intermolecular (non-covalent) interactions.<sup>[1]</sup>

Phthalocyanines (Pcs) are important photosensitizers in medical photodiagnosics and photodynamic therapy (PDT). An aggregation in polar media and a low solubility in water remain to be restrictions for the use of phthalocyanines at some applications. Crown-containing phthalocyanines are of interest as candidates for PDT. Crown ethers annulated<sup>[2]</sup> or introduced to a macrocycle through an oxygen bridge<sup>[3]</sup> (Figure 1) provide both higher solubility of macrocyclic compounds and self-assembling of Pc molecules with a guest cation. Ensemble stability is provided by the principle of geometrical conformity<sup>[4]</sup> and multiplicity of interaction, *i.e.*, an increase in the number of reacting groups.

One of possibilities to prevent the aggregation of Pcs in water is the use of surfactants, whose molecules are capable of self-organizing and forming various supramolecular structures. For example, octa[(4'-benzo-15-crown-5)-oxy]phthalocyanines are solubilized in aqueous solutions of anionic sodium dodecyl sulfate to form monomers and dimers at the SDS concentration close to the critical micelle concentration (*cmc*) and lower, respectively.<sup>[5-7]</sup> Supramolecular complexes (*guest-host*) are formed as a result of Na<sup>+</sup> coordination by the cavity of 15-crown-5 ether. Due to the compatibility of the cavity size and ionic radius of Na<sup>+</sup>, the presence of the latter in solution prevents the cation-induced aggregation of crown-containing Pc.<sup>[2]</sup> Their further organization in aqueous solutions will be determined by the properties of a solubilizing agent.<sup>[5,6]</sup> In micellar systems based on non-ionic surfactants, self-organization of tetraazachlorins was also studied.<sup>[8]</sup> Some amphiphilic polymers influence on porphyrin state in an aqueous environment and, as a result, increase their photodynamic action.<sup>[9]</sup>

Herein, we report on the solubilization and spectroscopic behaviour of a model compound, magnesium octa[(4'-benzo-15-crown-5)-oxy]phthalocyaninate (Mgcr<sub>8</sub>Pc), in the presence of polyelectrolytes (PEL) or their complexes with surfactants in water. PSS and PAH were used as polyelectrolytes, whereas anionic surfactants were SDS, SDBS and biocompatible SDC. Lysine hydrochloride and nonionic surfactant Triton X100<sub>red</sub> were also used (Figure 1). PSS is used in pharmaceuticals as a cation exchanger, and biodegradable SDC is considered as a potential system for drug delivery. At the same time, biocompatible SDC is poorly known as a solubilizing and gelling agent for Pc.<sup>[10,11]</sup>

## Abbreviations

SDS	sodium dodecyl sulfate
SDBS	sodium dodecylbenzene sulfonate
SDC	sodium deoxycholate
PSS	sodium polystyrene sulfonate
PAH	poly(allylaminehydrochloride)
lys-HCl	lysine hydrochloride
PEL	polyelectrolyte
Triton X100 <sub>red</sub>	Triton X100 reduced

## Experimental

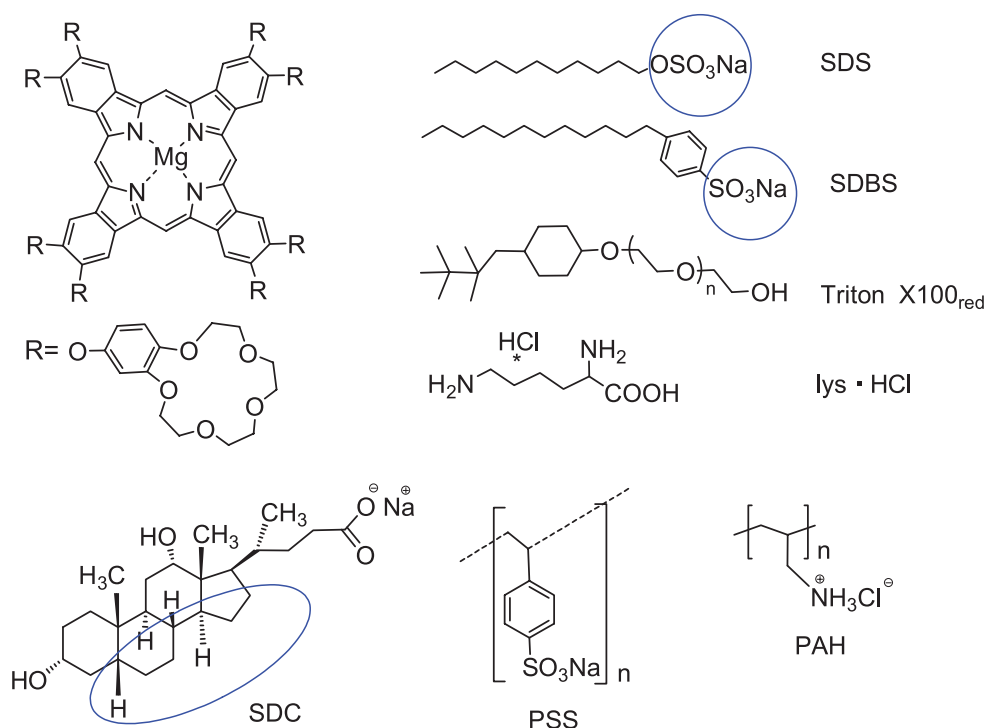
Magnesium octa[(4'-benzo-15-crown-5)oxy]phthalocyaninate was synthesized as described.<sup>[6]</sup> PSS (Aldrich, molecular weight 1000 kDa), PAH (Aldrich, molecular weight 15 kDa), Triton X100<sub>red</sub> (Aldrich), SDS (Aldrich, 98 %), SDBS (Aldrich, 95 %), SDC (Aldrich, 98 %), lys-HCl (≥99 % purity) and NaCl (for electrochemistry) were used as received. Twice distilled water was used for all preparations in aqueous solutions. Dichloromethane (Aldrich, spectrophotometrically grade) was distilled prior to use.

*Mgcr<sub>8</sub>Pc-PSS (PAH) solutions.* Powdered Mgcr<sub>8</sub>Pc was dissolved in an aqueous solution of PEL (PSS or PAH), which was then centrifuged. Solutions were allowed to equilibrate at room temperature. The attainment of the absorbance constant value was defined by registration of absorption spectra immediately after the preparation of samples and during their storage. It was also used at the fluorescence study. When conducting spectral measurements, the weighed amount of PSS, SDS (or SDC) and NaCl were successively added to the cell with Mgcr<sub>8</sub>Pc solution of the known concentration. The samples were stored in a dark place.

## Methods

Steady-state fluorescence spectra for solutions and hydrogels were collected by using a Perkin Elmer LS55 spectrofluorimeter in air at room temperature. Quartz cuvettes with a cell length of 1.0 cm were used. The spectral slit width for excitation and emission was set at 10.0 nm with an angle detection of 90°. Excitation and emission spectra were measured at λ<sub>em</sub> = 704 or 683 nm, and λ<sub>exc</sub> = 614 nm, respectively. The position of the emission band was independent of the excitation wavelengths (614, 625 or 635 nm) used. They lie in the field of the satellite peak and in close proximity to an absorption maximum of a long-wave Q-band. This should provide the maximal value of fluorescence intensity. Bands of light scattering on particles of a micro-heterogeneous media were not observed also.<sup>[12]</sup> No fluorescence was observed at all control experiments, and each blank experiment has contained the necessary background components at the same concentration as the sample. Absorption spectra detected after Pc excitation have retained the shape and intensity of the bands.

Absorption spectra in the UV-visible region were carried out on a Specord M-40 spectrophotometer (Carl Zeiss, Jena) using 1–10 mm rectangular quartz cells at room temperature. Some spectra were decomposed into Gaussian components using the Origin mathematic program package.



**Figure 1.** Structural formulas for magnesium octa[(4'-benzo-15-crown-5)oxy]phthalocyaninate, surfactants, polyelectrolytes and lysine hydrochloride. Polar groups for SDS and SDBS and a hydrophobic part for SDC are marked (see footnotes for abbreviations). Triton X100<sub>red</sub> is Triton X100 in the reduced (hydrogenated) form.

## Results and Discussion

The absorption spectrum for  $Mgcr_8Pc$  in dichloromethane shows a set of bands at the UV-visible range: a broadened N-band at 288 nm and the Soret band at 360 nm, the intense narrow Q-band at 690 nm ( $lg\varepsilon = 5.21$ ) and vibronic bands from the side of shorter wavelengths.<sup>[6]</sup> The spectrum is typical of the metallophthalocyanine monomer.

### *Magnesium Octa[(4'-benzo-15-crown-5)oxy]phthalocyaninate in Water*

Figure 2a shows the spectrum of  $Mgcr_8Pc$  in aqueous solution. In contrast to the narrow Q-band characteristic of the  $Mgcr_8Pc$  monomer, a broad Q-band at the 630–750 nm range agrees with Pc aggregation. The solution remains unchanged upon prolonged storage.<sup>[6]</sup> Pcs bearing a crown ether group are present in an aqueous NaCl solution only as aggregates of uncertain composition or even as unstable suspension.<sup>[6,13]</sup>

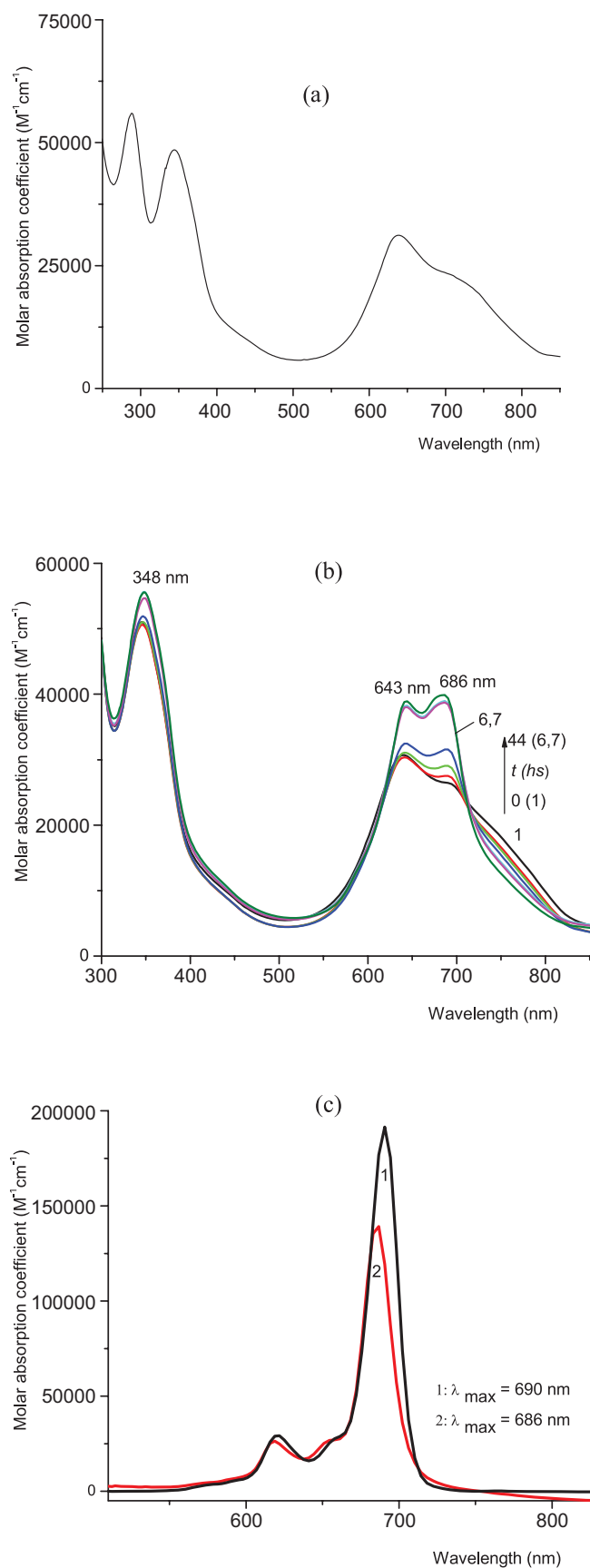
In the presence of strong polyelectrolyte PSS ( $cmc$  equal to  $1.8 \cdot 10^{-4}$  M was reported),<sup>[14,15]</sup> an increase of the absorbance of the  $Mgcr_8Pc$  solution is accompanied by noticeable changes of the Q-band shape relative to an aqueous solution of Pc (Figure 2b). The observed increase of the absorbance can be due to a decrease in the number of highly aggregated  $Mgcr_8Pc$  particles. This results from the existence of an isosbestic point at 716 nm (Figure 2b). An increase of the concentration of PSS in the  $Mgcr_8Pc$ /PSS system affects sufficiently weakly the optical characteristics of the solutions. For each concentration of PSS, the

absorbance of the  $Mgcr_8Pc$  aqueous solution and the Q-band shape remain almost unchanged for a long time.

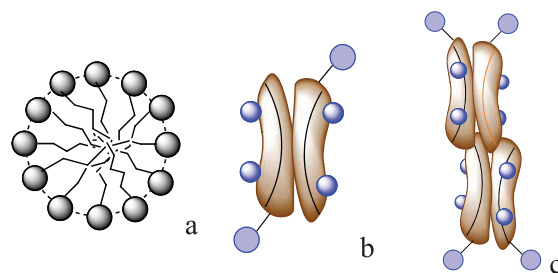
The addition of SDS to the  $Mgcr_8Pc$ /PSS solution ( $[SDS] = 0.011$  M is close to its  $cmc$ )<sup>[16]</sup> is accompanied by a rapid increase of the absorbance, wherein almost all Pcs transform into a monomeric form (Figure 2c). A similar behaviour is also characteristic of  $Mgcr_8Pc$  in Na-CMC/SDS and PSS/SDBS solutions. The spectral characteristics of the Pc monomer ( $\lambda_{max} = 686$  nm,  $lg\varepsilon = 5.15$ ) presented in a PSS/SDS solution are close to those for  $Mgcr_8Pc$  in  $CH_2Cl_2$  or an aqueous micellar solution of SDS.<sup>[6]</sup>

In contrast, the addition of sodium deoxycholate ( $[SDC] = 4.76 \cdot 10^{-3}$  M is close to its  $cmc$ )<sup>[17]</sup> to the  $Mgcr_8Pc$ /PSS solution leads only to a slight increase of the absorbance. Anionic surfactant SDC is specified by 'planar' diphilicity manifested in the formation of convex (hydrophobic) and concave (hydrophilic) surfaces. As a result, mechanisms of self-organization, micelle shape and size are essentially different for SDC and common micelle-forming surfactants such as SDS (Figure 3).<sup>[18,19]</sup>

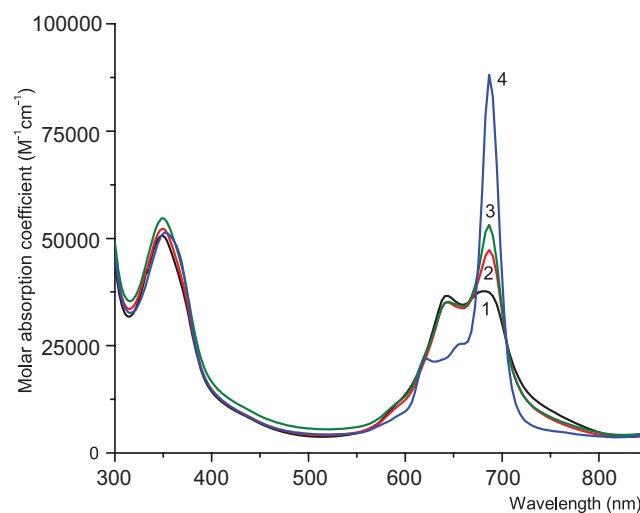
The effect of additives on the absorbance of aqueous solutions of  $Mgcr_8Pc$  is observed. When SDC is added to the  $Mgcr_8Pc$ /PSS solution, a small increase of the Q-band absorbance at the field of the monomer is already observed. Upon the next addition of NaCl, the Soret band in the UV-visible spectrum is bathochromically shifted ( $\sim 4$  nm), and an increase of the absorbance of the solution and simultaneous changes in shape and position of maximum of the long-wave Q-band are occurred (Figure 4). As a result, the spectrum observed is close to that shown in Figure 2c. On condition of simultaneous presence of NaCl and SDC in a solution



**Figure 2.** Absorption spectra of aqueous solutions of MgCr<sub>8</sub>Pc: additive free (a); spectral changes in the MgCr<sub>8</sub>Pc/PSS solution with time ([PSS] = const) (b); spectra of MgCr<sub>8</sub>Pc in dichloromethane (1) and in the presence of PSS/SDS (2) (c). Region of the Q-band is shown.



**Figure 3.** Schematic representation of the SDS micelles (a) and the aggregates (primary micelles) of SDC (b and c).



**Figure 4.** Absorption spectra of the MgCr<sub>8</sub>Pc aqueous solution in the presence of PSS (1), PSS/SDC (2,3) and PSS/SDC/NaCl (4); [MgCr<sub>8</sub>Pc], [PSS], [SDC] and [NaCl] are equal to  $1.54 \cdot 10^{-5}$ ,  $2.1 \cdot 10^{-2}$ ,  $4.76 \cdot 10^{-3}$ , and  $9.2 \cdot 10^{-2}$  M, respectively.

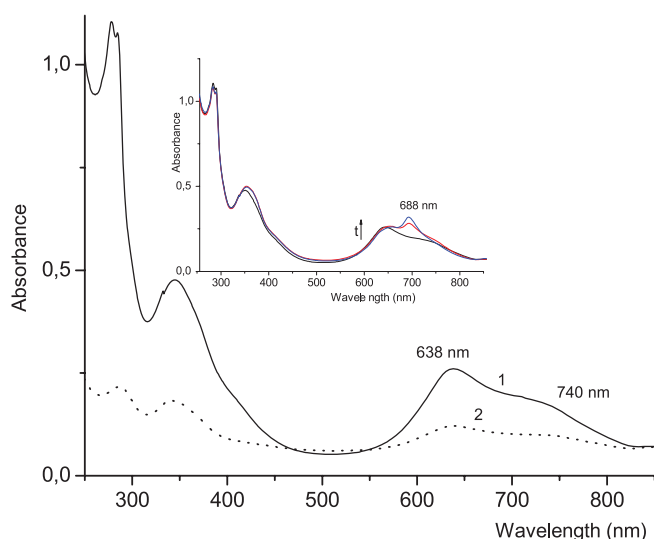
of MgCr<sub>8</sub>Pc/PSS, the sequence of their addition doesn't affect the final state of the system.

The behaviour of MgCr<sub>8</sub>Pc in the presence of anionic SDS, cationic PAH, neutral Triton X100<sub>red</sub> and the SDC/lys-HCl system is strongly different. So, the absorption spectra for MgCr<sub>8</sub>Pc in a solution of PAH or Triton X100<sub>red</sub> indicate an almost full aggregation of Pc (Figure 5) similarly to an additive-free aqueous solution (Figure 2a).

Thus, the aggregation of crown-containing Pc in aqueous solutions of Triton X100<sub>red</sub>, cationic PEL or surfactant (hexadecyltrimethylammonium bromide, for example) with the diameter of a polar 'head' essentially longer than that of the 15-crown-5 ether cavity indicates that only hydrophobic interactions are not enough to solubilize MgCr<sub>8</sub>Pc and to form its monomer in water.

The addition of anionic SDS to the MgCr<sub>8</sub>Pc/Triton X100<sub>red</sub> solution influences weakly on Pc, which has remained at the aggregated state predominantly (Figure 5, inset). The ability of SDS to monomerize MgCr<sub>8</sub>Pc in the presence of the second component, namely, PEL or nonionic surfactant, changes in water in the following sequence: PSS/SDS ≈ NaCMC/SDS ≫ Triton X100<sub>red</sub>/SDS (this work).

Figure 6 shows the absorption spectra (a) and a change of the absorbance of the MgCr<sub>8</sub>Pc aqueous solution in the



**Figure 5.** Absorption spectra of an aqueous solution of  $Mgcr_8Pc$  in the presence of Triton X100<sub>red</sub> (1) and PAH (2);  $[Mgcr_8Pc] = 1.13 \cdot 10^{-5}$  M,  $[Triton X100_{red}] = 14.3 \cdot 10^{-3}$ ,  $[PAH] = 23 \cdot 10^{-3}$  M. Inset: spectra of  $Mgcr_8Pc/Triton X100_{red}/SDS$  in time ( $[SDS] \sim 11 \cdot 10^{-3}$  M).

presence of lys·HCl and lys·HCl/SDC as a function of time (b). At a low concentration of lys·HCl (Figure 6b, region 1), the spectrum is almost identical to that of  $Mgcr_8Pc$  in an aqueous solution (Figure 2a) or in a solution of cationic PEL (Figure 5). When SDC is added to the  $Mgcr_8Pc/lys\cdot HCl$  solution, absorbance increases (Figure 6b, regions 2 and 3) as in the case of pure SDC.<sup>[10,11]</sup> However, the aggregation of Pc retains to a great extent in this case. The further addition of lys·HCl takes place already against the background of SDC ( $[SDC] > cmc$ ). It is seen that under these conditions

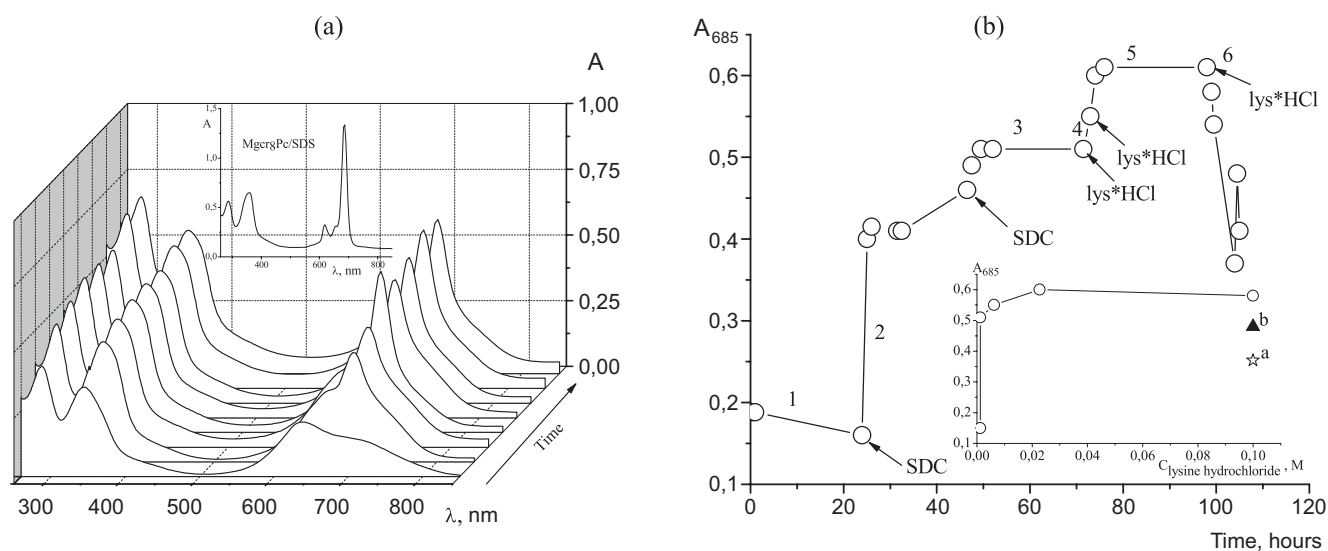
an increase in the concentration of lys·HCl leads to a slight increase of the absorbance (regions 4 and 5) with the absorption spectrum of  $Mgcr_8Pc/lys\cdot HCl/SDC/lys\cdot HCl$  close to the  $Mgcr_8Pc$  spectra in regions 2 and 3. The shift of the Q-band from 689 to 685 nm is observed in this case.

The absorption spectra of  $Mgcr_8Pc$  in the SDC/lys·HCl solution and in micellar solutions of SDS are markedly different (Figure 6a). This shows the difference in the Pc state, which is due to both the micellar organization of surfactants (Figure 3) and the presence of cationic lysine hydrochloride.

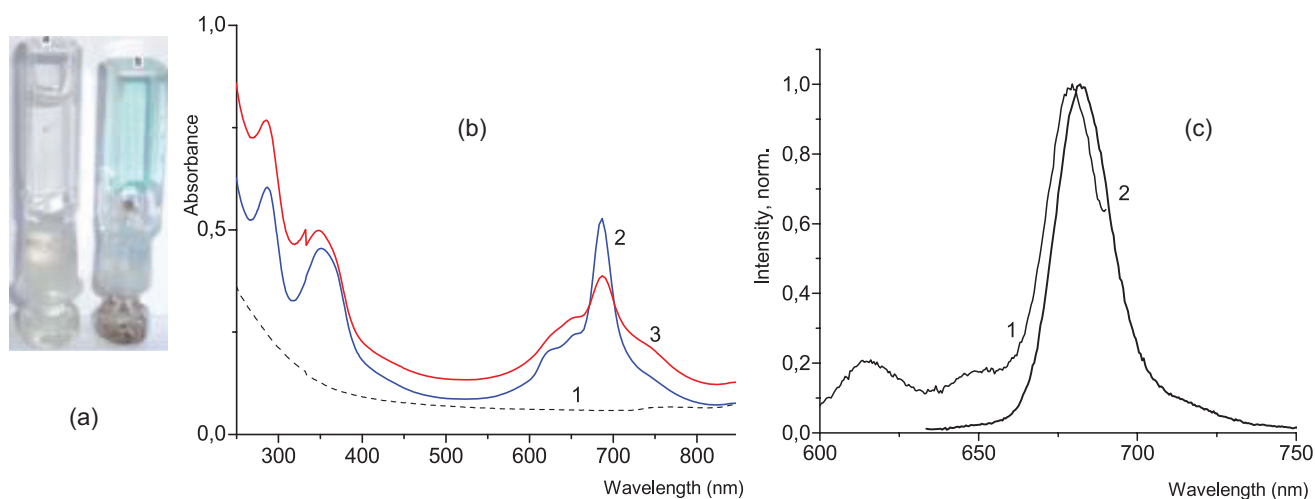
At the concentration of lys·HCl comparable with the concentration of NaCl, *i.e.*,  $\sim 0.1$  M (see above), the absorbance decreased at 685 nm has accompanied by the formation of a hydrogel (inset in Figure 6b). Rheology of the SDC/lys·HCl/ $Mgcr_8Pc/H_2O$  system differs from that of SDC/lys·HCl/ $H_2O$ . For the former system, this is a quite dense gel in which  $Mgcr_8Pc$  is distributed uniformly, and for the latter system this is a viscous liquid (Figure 7a).

Although in the number of the Gaussian components and the position and shape of the Q-band, the spectrum for Pc in the hydrogel is similar to the spectrum for a solution of  $Mgcr_8Pc/SDC/lys\cdot HCl$  (Figure 7b), there is one important difference, namely, the concentration of the  $Mgcr_8Pc$  monomer (Figure 8). Gel formation based on  $Mgcr_8Pc/SDC/lys\cdot HCl$  is a thermo-reversible process (Figure 8). At present supramolecular hydrogels based on small molecules are widely investigated.<sup>[20-23]</sup>

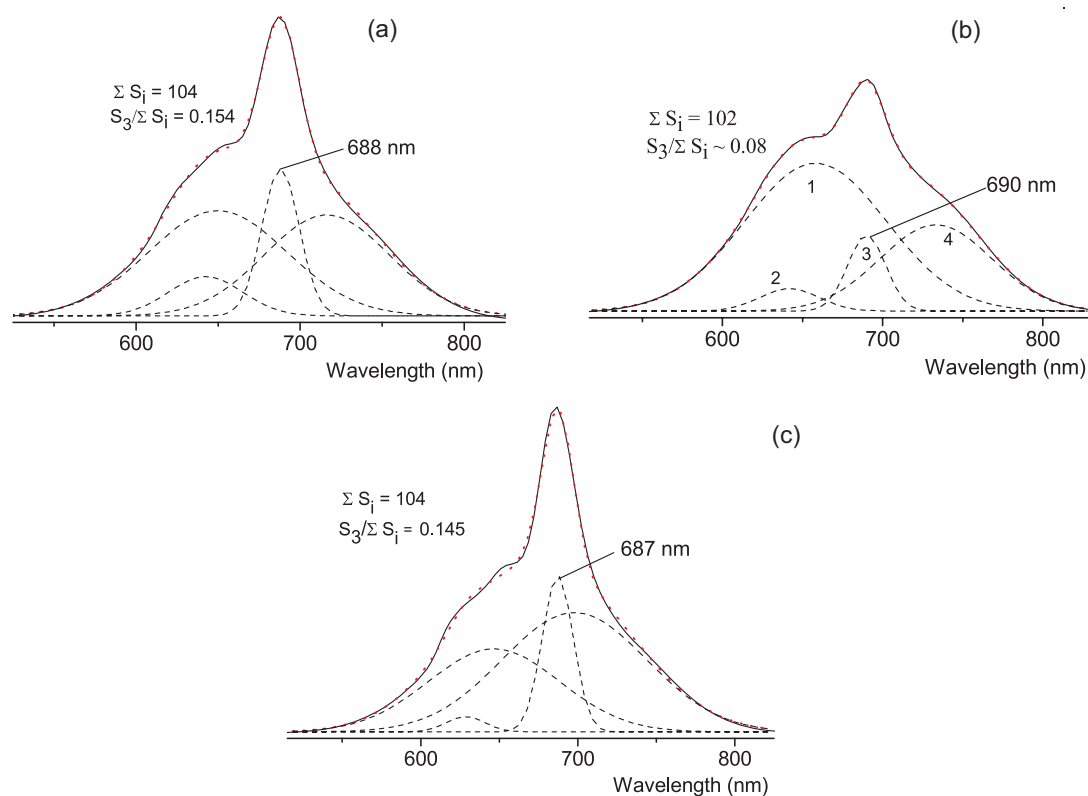
As seen from the spectra presented on Figure 7b and Figure 8, an aqueous solution of  $Mgcr_8Pc/SDC/lys\cdot HCl$  and hydrogel of the same composition are specified by a high degree of Pc aggregation in contrast to the  $Mgcr_8Pc/SDC/NaCl$  system at  $[SDC] > cmc$  and  $[NaCl] \sim 0.1$  M, where  $Mgcr_8Pc$  is present mainly as a monomer.<sup>[10]</sup> This indicates again an important role of  $Na^+$  ions in the formation of micelle-



**Figure 6.** Absorption spectra (a) and changes of  $Mgcr_8Pc$  absorbance ( $[Mgcr_8Pc] = 8.56 \cdot 10^{-6}$  M) in an aqueous solution with time (b) upon the addition of lys·HCl (region 1,  $[lys\cdot HCl] = 1.25 \cdot 10^{-3}$  M), sodium deoxycholate (regions 2 and 3,  $[SDC] = 9.9 \cdot 10^{-3}$  M and  $21.7 \cdot 10^{-3}$  M, respectively,  $[lys\cdot HCl] = 1.25 \cdot 10^{-3}$  M), lys·HCl (regions 4, 5 and 6,  $[lys\cdot HCl] = 6.2 \cdot 10^{-3}$  M,  $22.7 \cdot 10^{-3}$  M and 0.1 M, respectively,  $[SDC] = 21.7 \cdot 10^{-3}$  M). Spectrum of  $Mgcr_8Pc$  in micellar solution of SDS is given for comparison (Figure 6a, insert). Inset (Figure 6b):  $A_{685}$  vs lys·HCl concentration. Points (a) and (b) correspond to the absorbance of a hydrogel sample at room temperature and  $\sim 35^\circ C$ , respectively.



**Figure 7.** (a) The pictures of the SDC/lys-HCl viscous solution (left) and Mgcr<sub>8</sub>Pc/SDC/lys-HCl hydrogel (right); (b) Absorption spectra in aqueous media: SDC/lys-HCl solution (1), Mgcr<sub>8</sub>Pc/SDC/lys-HCl solution (2) and Mgcr<sub>8</sub>Pc/SDC/lys-HCl hydrogel (3); (c) Normalized excitation and emission spectra of the Mgcr<sub>8</sub>Pc/SDC/lys-HCl hydrogel at  $\lambda_{em} = 704$  (1) and  $\lambda_{ex} = 614$  nm (2), respectively.



**Figure 8.** Spectral changes in the absorbance of Mgcr<sub>8</sub>Pc/SDC/lys-HCl system with temperature (water as a medium): (a) – solution ( $\sim 50$  °C), (b) – gel (20 °C), (c) – solution ( $\sim -50$  °C).  $\Sigma S_i$  and  $S_3/\Sigma S_i$  are a sum of areas of Gauss components and ratio of area peak related to the Pc monomer ( $S_3$ ) to a  $\Sigma S_i$ , respectively.

bound monomers, particularly, Mgcr<sub>8</sub>Pc, in the solubilization of 15-crown-5 containing Pc by anionic surfactants. Similar geometric parameters of the Na<sup>+</sup> cation and 15-crown-5 ether cavity provide the formation of *guest-host* complexes as the simplest supramolecular structures. The formation of such complexes in the case of crown-containing Pc was confirmed by <sup>1</sup>H NMR interaction between Pc with annulated crown groups and Na<sup>+</sup> ions in an organic solvent.<sup>[24]</sup>

#### *Fluorescence of Mgcr<sub>8</sub>Pc, Mgcr<sub>8</sub>Pc/PSS, Mgcr<sub>8</sub>Pc/PSS/NaCl and Mgcr<sub>8</sub>Pc/PSS/NaCl/SDC Systems in Water*

According to the absorption spectra, Mgcr<sub>8</sub>Pc exists almost completely in the aggregated state in an aqueous solution (Figure 2a). No fluorescence was observed for aggregated Pc and the background components, respectively (Figure 9b, curves 1–3). The Mgcr<sub>8</sub>Pc excitation spectrum

for different Pc-solubilizing systems is almost similar to the absorption spectrum for the Pc monomer (Figure 9a, insert). The emission spectrum is shifted relatively to the excitation spectrum by  $\sim 5$  nm.

The changes shown in Figure 9b indicate that the fluorescence of  $Mgcr_8Pc$  is really pronounced in the PSS solution (Figure 9b, curve 4). Its intensity increases with the introduction of NaCl and SDC into the  $Mgcr_8Pc/PSS$  solution to attain the maximal value at the SDC concentration close to  $cmc_1$  in the presence of NaCl (Figure 9b, curve 6). Thus, these data indicate the appearance of the monomeric state of  $Mgcr_8Pc$  in the presence of PSS and the following growth of its concentration with increase of ionic strength of the solution and the introduction of SDC, since the Pc aggregates do not fluoresce.<sup>[25,26]</sup>

For  $Mgcr_8Pc/lys\cdot HCl/SDC$  in a hydrogel and solution, a low concentration of the  $Mgcr_8Pc$  monomer is identified spectrally ( $\sim 7$  and 15 %, respectively, Figure 8), and weak fluorescence is also observed (Figure 7c). In the presence of the cationic PEL,  $Mgcr_8Pc$  is completely aggregated in the aqueous environment, and no fluorescence is observed under excitation by light with  $\lambda = 614$  nm.

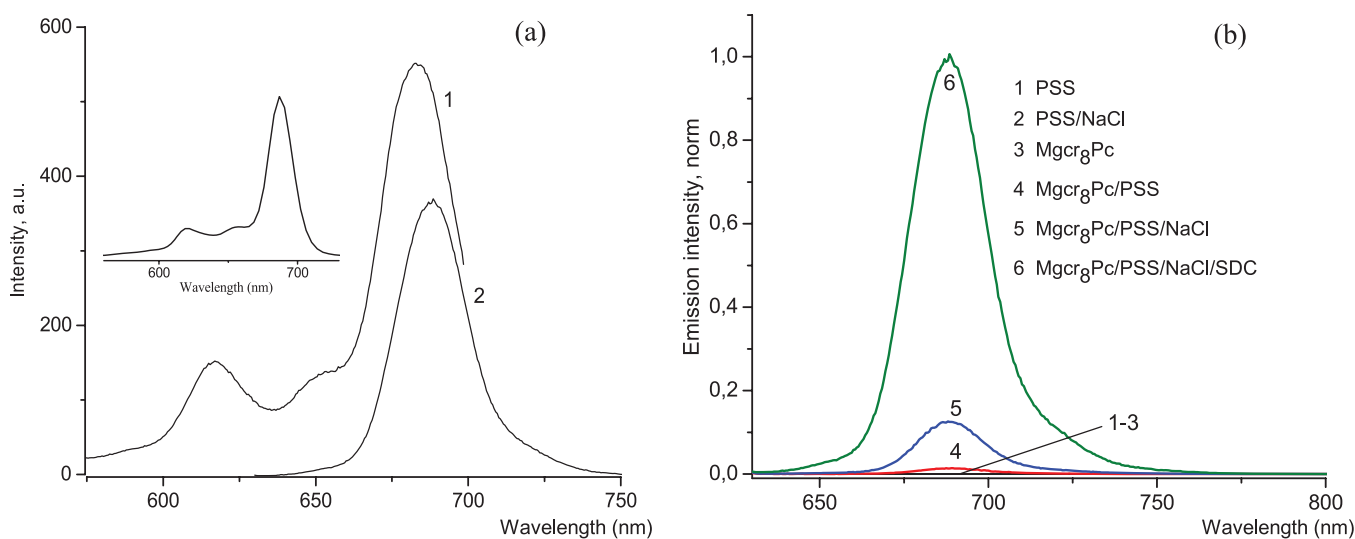
### Supramolecular Organization of $Mgcr_8Pc$ in Aqueous Environment in the Presence of Polyelectrolytes and Anionic Surfactants

The state of  $Mgcr_8Pc$  in organized micro-heterogeneous systems based on surfactants and PEL depends on the structural and charge factors of the latter. Because of structural differences (Figure 1), the shape and size of micelles are noticeably different for SDC and conventional micelle-forming surfactants, particularly, SDS (Figure 3). So, the  $Mgcr_8Pc$  monomer exists in micellar solutions of anionic SDS and SDBS.<sup>[6,10,27]</sup> In contrast, an increase of the ionic strength of a solution is already required for sodium

deoxycholate at the SDC concentrations significantly exceeding  $cmc$ .<sup>[10,11]</sup>

This work is based on the idea of the influence of electrolyte on critical micelle concentration of surfactants and configuration of a polymer chain. Poly(styrene sulfonate) is one of the simplest polyelectrolytes, which has been shown to possess hydrophobic properties as well. For PSS as well as other similar PEL, water is a good solvent. Therefore, in the absence of salt, PSS chains are essentially expanded and swollen.<sup>[28,29]</sup> With increase of ionic strength, PSS molecules 'shrink' to a more compact configuration due to a shielding effect of salt cations accompanied by decrease<sup>[30]</sup> of hydrodynamic radius ( $R_H$ ) of the polyelectrolyte coil,<sup>[31,32]</sup> 'ejecting' a portion of solvent (water) and probably forming nonpolar regions. In combination with the formation of a supramolecular *guest-host* complex between  $Na^+$  and a cavity formed by ethylene units and oxygen atoms of the crown ether in  $Mgcr_8Pc$ , the generation of nonpolar (hydrophobic) regions in PSS provides an increase of the absorbance of the Q-band at  $\lambda \sim 680$  nm (spectral region of Pc monomer) even in the presence of single PSS. The optical density of the  $Mgcr_8Pc/PSS$  solution increases by the subsequent addition of NaCl, indicating the magnification of  $Mgcr_8Pc$  monomer concentration. However, almost full monomerization of  $Mgcr_8Pc$  is achieved only in the presence of PSS, NaCl and SDC at the surfactant concentration close to  $cmc_1$ . In this case, the position of the Q-band of Pc in a PSS/NaCl/SDC solution is close to its position in dichloromethane or micellar solutions of conventional anionic surfactants (Figure 2c). It should also be noted that the presence of PSS provides a lower concentration of SDC required for the monomerization of  $Mgcr_8Pc$  compared to SDC only.<sup>[10]</sup> This suggests the synergistic effect of SDC and PSS for the  $Mgcr_8Pc$  monomerization.

In the given systems the position of the maximum of the Q-band for the micelle-bound  $Mgcr_8Pc$  monomer is slightly different. For example, the absorption spectrum



**Figure 9.** Spectra of  $Mgcr_8Pc$  in aqueous solution of PSS upon introducing NaCl and sodium deoxycholate.

(a) Excitation (1) and emission (2) spectra at  $\lambda_{em} = 704$  nm and  $\lambda_{exc} = 614$  nm, respectively ( $[Mgcr_8Pc] = 2.76 \cdot 10^{-6}$  M,  $[PSS] = 0.024$  M,  $[SDC] = 5.64 \cdot 10^{-3}$  M,  $[NaCl] = 0.098$  M); insert: absorption spectrum for the  $Mgcr_8Pc/PSS/SDC/NaCl$  system ( $[Mgcr_8Pc] = 2.76 \cdot 10^{-6}$  M,  $[PSS] = 0.024$  M,  $[SDC] = 5.64 \cdot 10^{-3}$  M,  $[NaCl] = 0.098$  M); (b) Effect of PSS, NaCl and SDC on the fluorescence intensity of  $Mgcr_8Pc$  ( $[Mgcr_8Pc] = 2.76 \cdot 10^{-6}$  M).

for the MgCr<sub>8</sub>Pc/SDC/NaCl system is specified by a greater hypsochromic shift of the Q-band as compared to micellar solutions of SDBS and SDS (6 and 4 nm, respectively) relative to the Q-band of the MgCr<sub>8</sub>Pc monomer in CH<sub>2</sub>Cl<sub>2</sub>. Nevertheless, close polarity of the environment formed around the MgCr<sub>8</sub>Pc molecules can be assumed, which is necessary for the existence of Pc mainly as a monomer in organized micro-heterogeneous aqueous systems based on anionic surfactants and/or PEL. Recently it was shown that the monomerization of MgCr<sub>8</sub>Pc is possible provided by synergism of different noncovalent interactions including the interaction of aromatic protons of MgCr<sub>8</sub>Pc with protons of the aliphatic chain of SDS, respectively.<sup>[6]</sup> The presence of the latter evidences for MgCr<sub>8</sub>Pc being in a hydrophobic environment in the micro-heterogeneous SDS medium.

## Conclusion

The behaviour of MgCr<sub>8</sub>Pc (model compound) in aqueous solutions of polyelectrolytes or their mixtures with anionic (sodium dodecyl sulfate, sodium dodecylbenzene sulfonate and biocompatible sodium deoxycholate) surfactants was investigated by spectral methods to find conditions for the existence of octa[(4'-benzo-15-crown-5)-oxy]phthalocyanines as monomers in the aqueous environment.

The partial and close to the full monomerization of MgCr<sub>8</sub>Pc in aqueous solutions has been achieved in the presence of single sodium poly(styrene sulfonate) and its mixture with biocompatible SDC in the presence of NaCl, respectively.

The formation of the supramolecular fluorescent hydrogel including MgCr<sub>8</sub>Pc was shown for the first time. In the MgCr<sub>8</sub>Pc/SDC/lys-HCl system, the gelling process is thermo-reversible. The solution and gel differ in the MgCr<sub>8</sub>Pc monomer concentration.

In all cases, the existence of MgCr<sub>8</sub>Pc as a micelle-bound monomer has been confirmed by the increase of the emission intensity, since aggregates and H-dimers of Pc do not fluoresce. It is suggested that the effect of SDC and PSS at the Pc monomerization is synergistic. Studies of photochemical and photophysical properties of crown-containing Pc in micro-heterogeneous media are in progress.

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Received 14.10.2015

Revised 27.11.2015

Accepted 14.12.2015