Liquid-phase systems with specified properties based on water-soluble derivatives of cobalt (II) phthalocyanine

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Abstract. In this work a wide range of sulfo derivatives of cobalt phthalocyanine was used as an example for the creation of liquid-phase systems with specified parameters. The role of the spacer bridge in the peripheral position of the macrocycle on its aggregation and coordination properties is illustrated. It was found that associated forms (H-associates) of sulfonated metal phthalocyanines, in which the ionic peripheral group is removed from the macrocycle by oxynaphthyl-oxyphenylazo-fragments (CoTSPc2 and CoTSPc3, respectively), have absorption in the region of 620-630 nm, while the Q-band of the monomeric form is located in the region 680-700 nm. It is shown that in the concentration range of 10^{-5} - 10^{-4} M the change in the optical density for CoTSPc1 and CoTSPc2 is described by a linear law. Based on the position of the absorption maxima of the Q-band, phthalocyanines are in an aggregated form in the form of H-aggregates. The study of the coordination properties of macrocycles was carried out with the addition of bidentate DABCO molecule. The stability of monoligand complexes with DABCO in aqueous solution changes in the order CoTSPc1 > CoTSPc3 > CoTSPc2.

1. Introduction
The oil contains low molecular weight mercaptans which have high toxicity and volatility, obnoxious odor, corrosivity. It is well known that toxic sulphurous-alkaline wastewater is formed during the processing of sulphurous oils and gas condensates. Therefore, during the extraction, transportation, storage, etc. there are big environmental and technological problems. One of the ways to clean oil from sulfur-containing compounds is deodorizing oil cleaning.

Phthalocyanines (Pcs) are structurally related to other tetrapyrole macrorcycles including porphyrins (the best known are chlorophyll and blood heme) and porphyrazines. Nowadays phthalocyanines are widely used in commerce as dyes and pigments, medical components, etc. [1–4]. An important application of tetrapyrolemacrocycles is their use in catalysis [5–8]. Metal complexes of phthalocyanines can act as effective catalysts in deodorizing oil purification [9]. Thus, sulfur-containing compounds such as mercaptans, sulfides, sulfites and thiosulfates of alkali metals are by-products of industrial processes and pollutants of waste and natural water. To solve the problem of environmental pollution, it was proposed to use the process of complete oxidation of sulfur-containing compounds before their discharge into wastewater. The possibility of participating in the catalytic process mainly depends on the electronic structure of the phthalocyanine complex, as well as on the central metal ion. The second factor plays a key role in the success of such reactions. For example, complexes with metal ions with an open d-shell, namely Co(II), Fe(II), Mn(II), have shown themselves to be effective catalysts for the oxidation of sulfur-containing compounds [10–12].
The ability of phthalocyanine complexes coordinate additional molecules in the fifth and sixth position of metal-complexing agent is crucial when considering their catalytic activity [13]. An important feature of such macrocycles is the ability of self-association in solutions and crystals, where the formation of ordered structures due to non-covalent interactions is possible, for example, H-, J-, T-type aggregates. At the same time, self-association significantly reduces the catalytic activity of macrocycles due to the closure of the reaction center of the macrocycle. The addition of coordinating ligands of different nature can dramatically increase the activity of the catalyst [14].

Varying the substituents in the peripheral/non-peripheral positions of the phthalocyanine molecule allows one to regulate the physicochemical properties. The processes of self-assembly of metal phthalocyanines in solutions can be controlled by changing the structure, primarily, the periphery of the macrocyclic complex and varying the parameters of the medium. The most promising is a combination of structural and coordination methods for regulating associative equilibrium in liquid-phase systems based on metal complexes of phthalocyanines, which allows maintaining the properties of a macrocycle.

The aim of this work is to reveal the role of the peripheral environment of the Co(II) phthalocyanine complexes on the aggregation and coordination properties upon the addition of the bidentate DABCO molecule, which, in turn, is necessary to obtain liquid-phase materials with the desired properties for catalysis.

2. Experimental part

The synthesis of the compounds CoTSPc1, CoTSPc2, and CoTSPc3 was carried out according to the procedures [15–17] respectively.

Dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF) solvents were purified and stored as recommended [18].

1,4-diazabicyclo[2.2.2]octane (DABCO) (Sigma-Aldrich) was used without additional purification.

Electronic absorption spectra (UV-Vis spectra) were recorded in the spectral range of 400-900 nm on Unico-2800 spectrophotometer (USA) in quartz cuvettes 10 mm thick.

Spectral studies were performed for isomolar series of solutions. The calculation of the stability constant upon the formation of the molecular complex of phthalocyanine with the ligand was carried out on the basis of the change in the absorption density of the solution in the region of the Q-band, according to [19]:

\[ K = \frac{[nL \cdot \text{CoTSPc}]}{[\text{CoTSPc}] [L]} \] (1)

The equilibrium concentration of the molecular complex was calculated as:

\[ c_{\text{CoTSPc-L}} = c_{\text{CoTSPc}}^0 \frac{(A_0 - A_c)}{(A_0 - A_s)} \] (2)

where \( c_{\text{CoTSPc-L}} \) – the equilibrium concentration of the molecular complex, \( c_{\text{CoTSPc}}^0 \) – the initial concentration of the macrocycle, \( A_0, A_c, A_s \) – the initial, the equilibrium and the final values of solution’s optical density of Q-band respectively. The concentration of the free ligand was determined by the equation:

\[ c_L = c_L^0 - c_{\text{CoTSPc}}^0 \frac{(A_0 - A_c)}{(A_0 - A_s)} \] (3)

Taking into account the above equilibria, the equation for calculating the stability constant takes the form:

\[ K = \frac{[A_0 - A_c]/(A_0 - A_s)]}{[c_L^0 - c_{\text{CoTSPc}}^0 \cdot (A_0 - A_c)/ (A_0 - A_s)]} \] (4)
The study was carried out under conditions of an excess of ligand with respect to metal phthalocyanine; therefore, the equilibrium concentration of the ligand was assumed to be equal to its initial concentration, which simplified the procedure for calculating $K_s$:

$$K_s = \frac{(A_0 - A_p)}{(A_0 - A_\infty) \cdot c_L^2}$$  \hspace{1cm} (5)

3. Discussion of results

Among the water-soluble derivatives of metal phthalocyanines, sulfonic acids are of particular interest, which is primarily due to their solubility in a wide pH range. Therefore, a number of water-soluble sulfonated cobalt-phthalocyanines, which have regularly changing peripheral substituents in their structure, were selected as the objects of study (Fig. 1).

Figure 1. Objects of research: Cobalt Tetra-4-(4-sulfo)phthalocyanine (CoTSPc1); Cobalt Tetra-4-[(6'-sulfo-2-naphthyl)oxy]phthalocyanine (CoTSPc2); Cobalt Tetra-4-[(4'-sulfo-phenyl)azo-4-phenoxy]phthalocyanine (CoTSPc3).

Metal phthalocyanines in aqueous media can be in monomeric and associated forms [20]. As a rule, dimeric and trimeric structures without the participation of solvent molecules in them are considered as associates [21].

$$\text{(CoTSPc)}_n \rightleftharpoons n\text{CoTSPc}$$  \hspace{1cm} (6)

At the first stage of the work, a comparative study of the associative state of the presented macrocycles in water was carried out. Electronic absorption spectroscopy is an important method for characterizing the intramolecular energy and the state of phthalocyaninemacrocycles in solution. Several types of bands are distinguished in the electronic absorption spectrum: the Q-band, caused by the transition of an electron from HOMO to LUMO, and also the B-band, where the electron passes from deeper occupied or vacant orbiters. The greatest attention is paid to the Q-type band ($\pi-\pi^*$-transition), since it is this band that is especially sensitive to changes in the $\pi$-system of the phthalocyanine macromolecule. Thus, based on the electronic absorption spectra (Fig. 2), in aqueous media CoTSPc1 forms associated structures in the form of H-dimers due to the overlapping of $\pi$-orbital clouds of two or more phthalocyanine molecules. During the formation of H-aggregates in the UV-Vis spectra, the absorption maxima undergo hypsochromic shifts in comparison with the initial monomer. It was found that associated forms of sulfonated metal phthalocyanines, in which the ionogenic group in the form of a sulfo group is removed from the macrocycle by a spacer oxygen bridge (CoTSPc2 and CoTSPc3, respectively), have absorption in the region of 620-630 nm, while the Q-band of the monomeric form is located in regions 680-700 nm, while stable H-associates are formed due to the overlap of the $\pi$-electron density of two macrocycles (Fig. 3, Fig. 5). The study of the concentration dependence for the considered macrocycles CoTSPc1 and CoTSPc2 in aqueous media showed observance of the Lambert-Bouguer law in the studied concentration range (Fig. 4). Thus, in the solution there is one kind of particles in the form of aggregated structures.
For CoTSPc3 (Fig. 5), upon dilution, a positive deviation from the Beer–Lambert–Bouguer law is observed (Fig. 5, inset). This is most likely due to aggregation processes, which are manifested to a large extent in comparison with CoTSPc1 and CoTSPc2.

**Table 1.** Extinction coefficients for aqueous solutions of cobalt phthalocyanine derivatives.

| macrocycle   | $\varepsilon_D$ (L/(mol·cm)) |
|--------------|-----------------------------|
| CoTSPc1      | 15200±100                   |
| CoTSPc2      | 4800±50                     |
| CoTSPc3      | 5200±60                     |

The investigated metal phthalocyanines in DMF and DMSO are monomeric (table 2). This is primarily due to the presence of a specific solvation interaction between the macrocycle and the environment. The coordinated solvent helps to compensate for the lack of electron density on the central metal cation, thereby preventing the formation of H-aggregates, including due to the geometric factor. In addition, DMF and DMSO, which have a high dielectric constant, will enhance ionization at
the periphery of the phthalocyanine molecule, which in turn leads to an increase in the Coulomb repulsion. The greatest effect is associated with cobalt tetrasulfophthalocyanine due to the geometric factor of the proximity of the peripheral substituent to the macroring.

Table 2. Extinction coefficients of monomeric forms of metal phthalocyanines in organic media.

| macrocycle     | $\varepsilon_{\text{M}}$ | DMSO         | DMF          |
|----------------|---------------------------|--------------|--------------|
| CoTSPc1        | 45000 ± 90                | 58400 ± 90   |              |
| CoTSPc2        | 18850 ± 60                | 24200 ± 90   |              |
| CoTSPc3        | 40560 ± 80                | 32360 ± 80   |              |

The use of individual molecules in the process seems to be a promising solution for obtaining the most efficient catalytic systems. For this purpose, the coordination properties of molecules were investigated, and liquid-phase systems based on a macrocycle and an organic bidentate ligand were obtained.

Table 3. Stability constants of molecular complexes of cobalt phthalocyanine derivatives and DABCO in aqueous media.

| macrocycle     | $K_s$, L/mol (1:1) |
|----------------|--------------------|
| CoTSPc1        | 13000 ± 100        |
| CoTSPc2        | 8500 ± 100         |
| CoTSPc3        | 18000 ± 250        |

A shift in associative equilibrium (6) is achieved with an increase in the concentration of the organic agent. Thus, when DABCO is added to the system, the intensity of the absorption band in the 630 nm region (absorption band of the dimer) and its bathochromic shift occur in the electronic absorption spectra of an aqueous solution of CoTSPc1. In this case, for the Q-band at 670 nm (absorption band of the monomer), a consistent increase in intensity is observed. The bathochromic shift of the Q-band by 8 nm and the presence of isosbestic points indicate the coordination of the DABCO molecule on the central metal cation, which leads to the dissociation of the π-π dimers of CoTSPc1.

For CoTSPc2, when DABCO is added to the system, an increase in the absorption intensity of the dimer band and its bathochromic shift by 30 nm are observed, while the band of the monomeric form in the region of 665-670 nm is not recorded. Similar results are observed for CoTSPc3. The stability constants of molecular complexes with DABCO are presented in Table 3.

4. Conclusions

For the use of phthalocyanines as catalysts for deodorizing oil purification, individual molecules are the most promising. The industry uses cobalt tetrasulfophthalocyanine (CoTSPc1). In solution, the macrocycle is in an aggregated state, which reduces the catalytic properties of the macrocycle. Substituted phthalocyanines in our work are also aggregated; however, as it was found in the process of molecular formation with DABCO, the resulting molecular complexes for CoTSPc2 have a much lower stability constant. This allows us to say that such systems are more labile and, in the course of catalysis, will make it easy to replace the ligand molecule with a substrate, for example, in the form of a sulfur-containing compound. Thus, liquid-phase systems based on phthalocyanine complexes and ligands are promising for obtaining the most effective catalysts for deodorizing petroleum purification. This prevents the closure of the reaction center of the macrocycle, which will lead to an increase in the catalytic activity of the complex.
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6. References
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