COMPLEX FORMATION OF 1,4-DIAZABICYCLO[2.2.2]OCTANE WITH COPPER(II) TETRASULFOPHTHALOCYANINE IN AQUEOUS SOLUTION

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The self-association in the formation of copper tetrasulfophthalocyanine complex and 1,4-diazabicyclo[2.2.2.]octane (DABCO) in aqueous solution are reported. Formation of phthalocyanine π-π dimers and a CuPc-DABCO complex could be confirmed, however, formation of sandwich-type dimers could not be detected.

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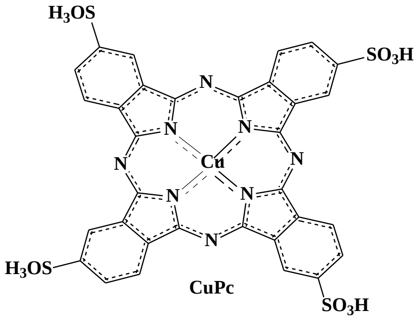
Introduction

Transition metal complexes of water-soluble phthalocyanine derivatives are used as high-performance catalyst in different oxidation processes in organic chemistry,[1-4] as photosensitizers in photodynamic therapy of cancer[5-7] and as inactivators of bacteria and virus.[8,9] Mechanisms of catalytic and biological action of such compounds are based on processes of molecular ligands coordination with central metal cation.[10,11]

Association of macromolecules in aqueous medium is the main trouble while using water solution of metalophthalocyanine. That process reduces their useful properties.[12-14] Linked π-electron system, that is located above and below the plane of the molecule, plays the main role in aggregation of metalophthalocyanines.[15,16] The central metal cation forming π-π dimer becomes isolated for ligand coordination. The second important factor affecting the associative balance is solvation.

It is possible to control the balance of monomer-dimer forms in water solution of metalophthalocyanines by changing the molecular complexation processes and solvating ability of medium.



Scheme 1. Structure of copper tetrasulfophthalocyanine complex

Associated form of copper metalophthalocyanine complex in water solution and its molecular complexation with 1,4-diazobisyclo[2.2.2]octane are reported.

Materials

Copper tetrasulfophthalocyanine (CuPc) is synthesized and purified by a known "direct sulfonation" method.[17] Its composition and structure is confirmed by electron-absorbtion spectroscopy, IR spectroscopy and elemental analyzes. IR-spectra were recorded on the Avatar 360 FT-IR spectrophotometer using KBr tablets. , There are intense bands at 700, 1032-1035, 1192-1197 cm^{-1}, it is caused by presence of sulfonic groups. Oscillation in 839-855 cm^{-1} is caused by C-H vibrations of three-substituted benzene nuclei connecting with porfirazine ring. IR-spectra matched with literature data.[18] UV-Vis spectra were recorded in the frequency range 400 – 4000 $cm^{–1}$.

Commercial product (DABCO) 1,4-diazabicyclo[2.2.2]octane (Sigma-Aldrich) with 99.98% purity was used without additional purification. Degased bidistilled water was used for preparing the solutions.

The coordination process of DABCO was studied spectrophotometrically. Electronic absorption spectra were recorded on a double-beam Shimadzu UV 1800 spectrophotometer. Investigations were carried out at 298.15 K using 10 mm quartz cuvettes, placed in a thermostatic cell.

Results and discussion

Association of metalophthalocyanine sulfonated derivatives in water solution is reported in the literature, which suggests[19-23] its ability to aggregate through the formation of dimers due to the overlap of π-electron systems of macrocycles. The thermodynamic parameters of associative monomer-dimer equilibrium in water-organic environment are also studied in this works.

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UV-Vis spectra of CuPc at different dilutions in water

$$2\mathrm{CuPc} \xrightleftharpoons{K_1} (\mathrm{CuPc})_2 \qquad (1)$$

(Fig.1), suggests dimerization of CuPc (c $2\cdot10^{-7}$ to $2\cdot10^{-4}$ mol L^{-1}) in water.

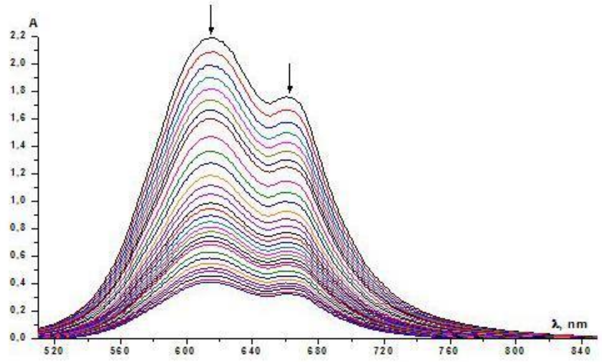

Figure 1. UV-Vis spectra's changing upon diluting of CuPc water solution ($c = 8\cdot10^{-4}$ to $2\cdot10^{-7}$ mol L^{-1}) at 298.15 K

Both dimeric and high-order associations are observed in aqueous solution. Associated forms of CuPc absorbs light in the 615-620 nm, monomeric forms (Q-band) in the 662-665 nm.[19,24] Changing ratio of intensities $\lambda_{620}/\lambda_{665}$ has a non-linear character. At the first stage there is a consistent increase of the ratio, it reflects the shift of equilibrium (1) to the monomerization of macrocycle. When the concentration of CuPc reaches about $3\cdot10^{-5}$ mol L^{-1}, the ratio becomes constant. This fact indicates equilibrium between monomeric and associated forms in process (1).

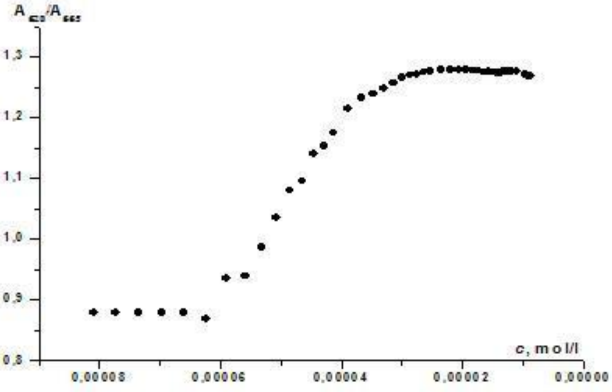

Figure 2. Ratio's changing of absorbing intensity of monomeric and dimeric forms of CuPc at 298.15 K

Analysis of literature data[15,16,20,24] and CuPc structure suggests formation of dimers due to the overlap of π-electron systems of two molecules. Formation of other types of associations , for example, due to coordinating interaction of distal substituent of phthalocyanine molecule with other macromolecule or μ-oxo-dimerization is unlikely because of coordinating features of central copper cation which is a part of macrocycle.

The molar extinction coefficient for the dimeric form of CuPc is $\varepsilon_D = 5000 \pm 80$ L mol^{-1} cm^{-1} and that of monomeric is $\varepsilon_M = 5900 \pm 80$ L mol^{-1} cm^{-1}. The closeness of the values of molar extinction coefficients suggests similarity in the light-absorbing source of macrocycle. It confirms π-π-dimerization. Coordination of ligand by molecule of dimer will promote a redistribution of electron density in the molecule of dimer, which, depending on the donor ability of the ligand, will have a significant effect on the association.

There are significant spectral changes during the titration of water solution of CuPc with solution of DABCO (Fig. 3). There is increase of Q-band absorption intensity and its bathochromic shift of 5 nm, although width of band stays wide enough. Intensity of absorption band of dimeric form (620 nm) is reduced.

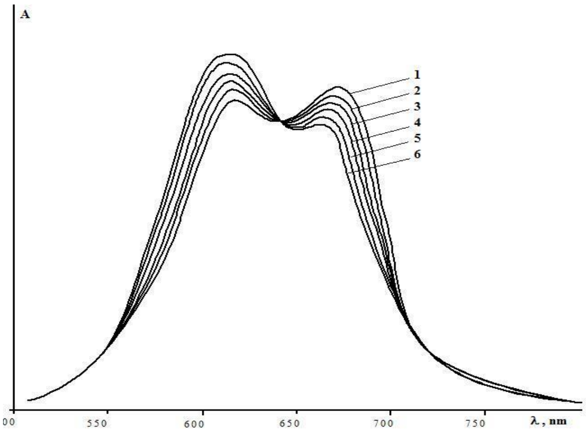

Figure 3. UV-Vis spectra's changing during titration of water solution of CuPc ($c = 6.99\cdot10^{-5}$ mol L^{-1}) with solution of DABCO (c=4.98·10-2 mol L^{-1})

It is known that tetrapyrrolic macroheterocyclic compounds are able to coordinate additional ligands, depending on the denticity. Formation of 1:1, 1:2, 2:1complexes is possible which can cause various spectral changes.[25-27]

In the present case, in addition to (1) the following equilibria can also be present.:

$$\mathrm{CuPc} + \mathrm{L} \xrightleftharpoons{K_2} \mathrm{CuPcL} \qquad (2)$$

$$\mathrm{CuPcL} + \mathrm{L} \xrightleftharpoons{K_3} \mathrm{CuPcL}_2 \qquad (3)$$

$$\mathrm{CuPcL} + \mathrm{CuPc} \xrightleftharpoons{K_4} (\mathrm{CuPc})_2\mathrm{L} \qquad (4)$$

In case of tetrapyrrolic macroheterocyclic compounds it is known that metal atom comes out of the plane of coordination node towards extra ligand when ligand is attached. Change in the geometry of the complex leads to a bathochromic shift in Q-band. There is a hypsochromic shift when the second ligand is coordinated. As a result of these factors, total shift of the Q-band of absorption could be small.[28]

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The obtained spectral data indicates that the equilibrium (1) shifts towards monomeric form when DABCO (L) is added due to the formation of monomolecular complex in (2). According the equation (5), the calculated stability constant (K_2) of molecular complex was 210 L mol^{-1}.

$$K_2 = \frac{[\mathrm{MPcL}]}{[\mathrm{MPc}]\cdot[\mathrm{L}]} = \frac{1}{[\mathrm{L}]}\cdot\left(\frac{\Delta A_{1,\lambda_1}\cdot\Delta A_{0,\lambda_2}}{\Delta A_{0,\lambda_1}\cdot\Delta A_{1,\lambda_2}}\right), \qquad (5)$$

where λ_1 = decreasing wavelength, λ_2 = increasing wavelength, [L]= equilibrium concentration of the ligand, ΔA_0 = maximum change in the optical density of solution at a given wavelength, ΔA_i = change of the optical density of solution at a given wavelength and given concentration.

Increase of DABCO concentration in solution to molar ratio CuPc:DABCO 1:50 does not lead to the formation of sandwich-type dimers (4).

According to the value of K_2, the molecular complex is not stable enough and equilibrium is shifted toward associated macrocyclic form that confirms the view of electronic absorption spectra. Formation of sandwich-type dimers requires a sufficient amount of phthalocyanine monomers. Therefore, the obtained data confirms the formation of CuPc dimers by π-π type.

π-π Dimers are formed due to π-σ-contraction effects and π-π-repulsion of electronic systems of two macromolecules. Coordination of DABCO should increase polarization of macrocycle π-system. It causes domination of π-π-repulsion processes over process of π-σ-contraction and shifts equilibrium (1) toward monomeric form, but there was no significant shift of associative equilibrium.

This fact may be explained in terms of competing of solvation interaction of water molecules with macrocycle and DABCO molecules. It is known,[29-31] that coordinated molecule of water, thanks to additional hydrogen bonds, could form solvation shell around macrocyclic molecule. After DABCO molecules enter in this shell, there is, probably, a resolvation, that is why CuPc dimer – DABCO coordination interaction is prevented.

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