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Peculiarities of solvation interaction of water-soluble metallophthalocyanines with ethanol

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Abstract

Physico-chemical characteristics of molecular complexes for water-soluble metallophthalocyanines with alcohol were obtained by the method of thermogravimetric analysis. The change of aggregation state of metallophthalocyanines in aqueous alkaline solutions which is due to the ethanol additions was explained taking into consideration the results of thermogravimetric analysis of metallophthalocyanines crystallosolvates with ethanol.

Keywords: Metallophthalocyanines; Aggregation; Molecular complexes

1. Introduction

The study of water-soluble metallophthalocyanines is of great theoretical and practical significance. More and more papers in which macroheterocycles mentioned above act as effective catalysts for the oxidation of phenols and sulfur containing substances [1], photosensors [2]. Photosensor and catalytic activity of water-soluble metallophthalocyanines depends on their aggregation state in solutions and it decreases many times [3,4] during the aggregation of metallophthalocyanines. That is why for successful practical application of water-soluble metallophthalocyanines it is necessary to solve the problems connected firstly with the state of the above mentioned macroheterocyclic substances in solutions. At present there are two ways of solving the problems of metallophthalocyanine aggregation; capsulating metallophthalocyanines in micelles, intercalating in polymeric matrixes, silica, etc [4,5] and the addition of detergents into phthalocyanine solution. The mechanism of the effect of detergents on the state of water-soluble metallophthalocyanines in solutions has not been studied sufficiently fully and the aim of the present work is to study the action of ethanol on the state of water-soluble metallophthalocyanines in aqueous alkali solutions and the study of the peculiarities of solvation interaction of metallophthalocyanines with ethanol. Sodium salts of carboxy- and sulfo-substituted complexes with cobalt(II), copper(II), aluminum(III), and zinc(II) were chosen as the objects of the study. The influence of the nature of a central metal and phthalocyanine macrocycle on the complex formation properties of metallophthalocyanines was studied taking into consideration the results of studying carboxy-substituted zinc(II)phthalocyanines [6].

2. Experimental

Sodium metallophthalocyanine salts of copper(II)tetra-4-carboxyphthalocyanine ($Cu(4\text{-}COONa)_4Pc$), copper(II)octa-3,5-carboxyphthalocyanine ($Cu(3,5\text{-}COONa)_8Pc$), cobalt(II)tetra-3-carboxyphthalocyanine ($Co(3\text{-}COONa)_4Pc$), cobalt(II)tetra-4-carboxyphthalocyanine ($Co(4\text{-}COONa)_4Pc$), zinc(II)tetra-4-sulfophthalocyanine ($Zn(4\text{-}SO_3Na)_4Pc$), aluminum(III)tetra-4-carboxyphthalocyanine ($HOAl(4\text{-}COONa)_4Pc$) were synthesized and purified in accordance with the recommendation [7,8].

Crystal samples were dried to constant weight in vacuum at 343–353 K in order to remove solvent molecules.

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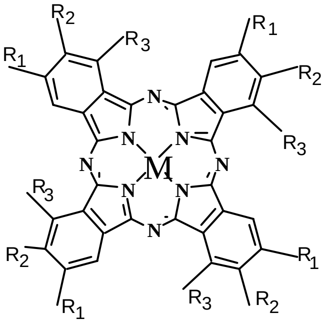

Cu(4-COONa)$_4$Pc: M=Cu, R$_1$=R$_3$=H, R$_2$=COONa;
Cu(3,5-COONa)$_8$Pc: M=Cu,R$_2$=H, R$_1$ =R$_3$=COONa;
Co(4-COONa)$_4$Pc: M=Co, R$_1$=R$_3$=H, R$_2$=COONa;
Co(3-COONa)$_4$Pc: M=Co, R$_2$=R$_1$=H, R$_3$=COONa;
Zn(4-SO$_3$Na)$_4$Pc: M=Zn, R$_1$=R$_3$=H, R$_2$=SO$_3$Na;
HOAl(4-COONa)$_4$Pc: M=Al(OH), R$_1$=R$_3$=H, R$_2$=COONa

Ethanol was dried by boiling in the presence of anhydrous $CuSO_4$. Then it was distilled twice over CaO. The drying was carried out in the presence of the metallic sodium. Distilled and deionized water was used in preparing the solutions.

The crystallosolvate samples were prepared from the aqueous alkaline solution of metallophthalocyanine and ethanol (3:1, v/v). The precipitate containing metallophthalocyanine was separated by centrifuging. After that it was placed into Soclet's device and conditioned for 5 h in the presence of ethanol vapors. Thermogravimetric studies were performed by a 1000D Model, MOM derivatograph (Hungary).

The data about thermal stability of metallophthalocyanine are necessary for the exact estimation of metallophthalocyanine crystallosolvate derivatograms with ethanol. The weighed sample amounted to 15–20 mg and the heating velocity was $5\,^{\circ}\mathrm{C\,min^{-1}}$ during the study of thermal stability of metallophthalocyanines. The study of the crystallosolvates was done in the weighed sample equal to 150–200 mg and the heating velocity was $0.6\,^{\circ}\mathrm{C\,min^{-1}}$. In the given paper as a theoretical base of the thermogravimetric study, the evaporating velocity–pressure of saturated solvent vapors relation is used. The pressure of saturated solvent vapors is sensitive to the conditions of evaporating molecules [8,9]. The thermogravimetric data were processed by means of the "Microsoft Excel" program. The program allowed determining the values of the straight-line slope angles. It also calculated the enthalpy of vaporization during the solvent evaporating out from the crystallsolvates. The correlation coefficient was not less than 0.998. The detailed description of the experimental procedure and the error calculations are given in paper [10].

The electronic absorption spectra were measured on a "Specord M40" spectrophotometer.

3. Discussion

3.1. Influence of ethanol on aggregation of metallophthalocyanines in solution

Water-soluble metallophthalocyanines are susceptible to the aggregation in aqueous solutions. The anionic metallophthalocyanines state in solutions is determined as a rule by $\pi-\pi$-binding between the aromatic systems of metallophthalocyanine molecules and the electrostatic repulsion of the periphery functional substituents. The $\pi-\pi$-dimerization of the water-soluble metallophthalocyanines causes substantial changes in the electronic absorption spectra of metallophthalocyanine solutions. Therefore, the most intensive Q-band in the visible region shifts towards the short-waves region. The electronic absorption spectra of metallophthalocyanine dimer (associate) partially overlaps the Q-band of monomer form of metallophthalocyanine. It completely screens the Q_x-satellite of the Q-band [11]. The overlapping of monomer and dimer metallophthalocyanine form spectra does not allow to estimate the percentage of a monomer and an associate by their intensity absorption bands ratio. The changes of the relation of absorption intensities of dimer (D) and monomer (M) Q-bands explain the equilibrium shifts in different directions.

$$\mathrm{M} + \mathrm{M} \Leftrightarrow \mathrm{D} \qquad (1)$$

The analysis of the electronic absorption spectra of the metallophthalocyanines ($10^{-6}\,\mathrm{mol\,kg^{-1}}$) determines presumably the monomer form of OHAl(4-COONa)$_4$Pc, Co(3-COONa)$_4$Pc, Cu(3,5-COONa)$_8$Pc in water–alkaline solutions, while Cu(4-COONa)$_4$Pc exists in aggregate forms and Co(4-COONa)$_4$Pc electronic absorption spectra include approximately equal amounts of monomers and associates [11]. The existence of OH-axial ligand of the HOAl(4-COONa)$_4$Pc molecule results in shifting the central Al^{3+} ion out from the macroring plane and deforming the phthalocyanine macroring [12]. Thereby it probably interferes with the effective $\pi-\pi$-interaction between the metallophthalocyanine molecules. The existence of Co(3-COONa)$_4$Pc and Co(3-COONa)$_4$Pc and Cu(3,5-COONa)$_8$Pc within water–alkaline solutions presumably in the monomer form, probably causes the injecting of the solid carboxylic group into the third position of macroring. It effectively interferes with $\pi-\pi$-interaction between phthalocyanine molecules. A similar conclusion was obtained before while analyzing the electronic absorption spectra of Zn(3-COONa)$_4$Pc in water–alkaline solutions [6].

The titration of metallophthalocyanines by ethanol in aqueous alkaline medium achieving the volume ethanol $NaOH_{aq}$ relation 0.3:1 in case of Zn(4-SO$_3$Na)$_4$Pc and

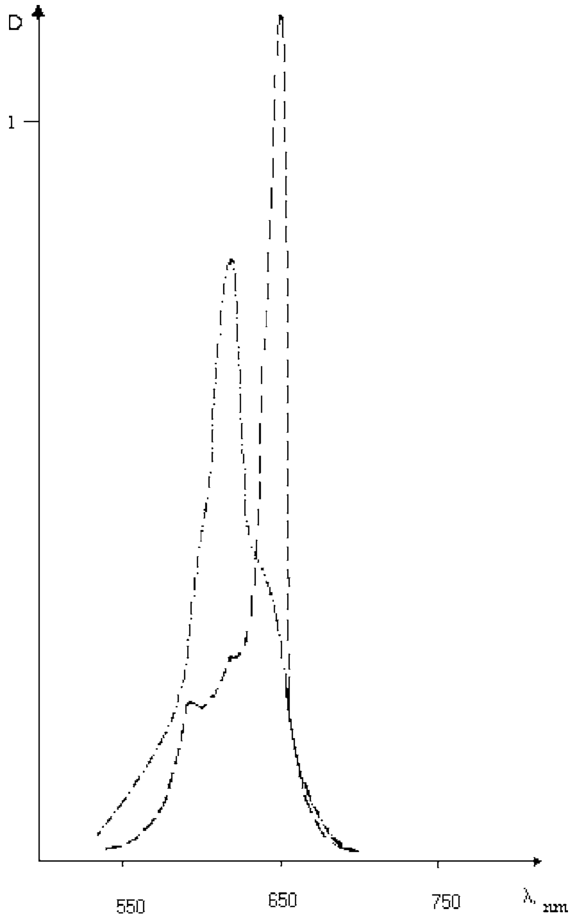

Fig. 1. The electronic adsorption spectra $Zn(4\text{-}SO_3Na)_4Pc$ in (—) water solutions (- - -) water–alkaline medium after ethanol addition (0.3:1, v/v).

$Zn(4\text{-}COONa)_4Pc$ as well [6] results in great spectral changes (Fig. 1). Taking into consideration the electronic absorption spectra of the substances given above the equilibrium (1) practically completely shifts to the formation of a monomer form (Fig. 1). In the case of copper(II)phthallocyanines the addition of ethanol results in the decrease of absorption intensity in the visible region but the relation of absorption intensity of a monomer and a dimer confirms the equilibrium shift towards the formation of monomers ($\lg\varepsilon_M/\lg\varepsilon d > 1$) (Fig. 2). On the contrary the absorption intensity in the electronic absorption spectra $HOAl(4\text{-}COONa)_4Pc$ practically is not changed but the left shoulder of Q-band disappears by $\lambda = 606$ nm. The addition of ethanol into aqueous–alkaline solutions of cobalt(II)phthalocyanines causes insignificant (2–3 nm) shift of absorption Q-band towards long-wave region.

The addition of a great amount of ethanol into aqueous alkaline solution of carboxylic substituted metallophthalocyanines results in their aggregation. Thus the spectral study being carried out allows to assume that the character of metallophthalocyanines interaction with alcohol depends on the nature of a central metal ion and a phthalocyanine macroring.

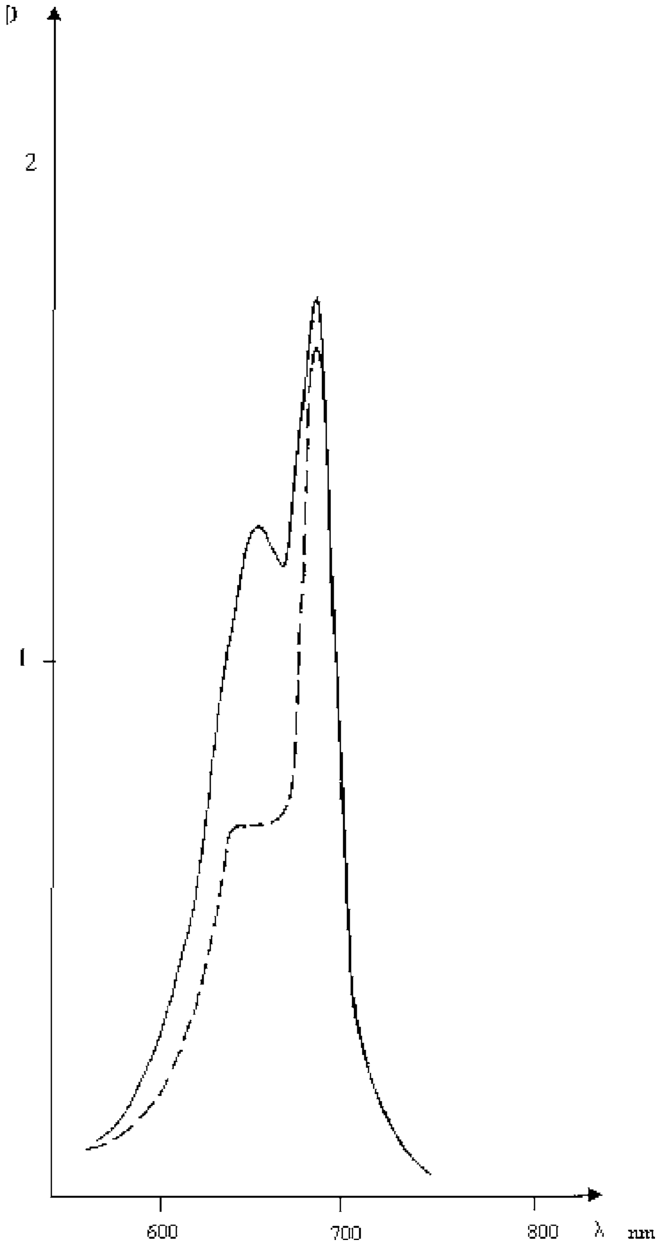

Fig. 2. The electronic adsorption spectra $Cu(3,5\text{-}COONa)_8Pc$ in (—) water solutions (- - -) water–alkaline medium after ethanol addition (0.3:1, v/v).

3.2. Specific interactions of metallophthalocyanines with ethanol

The quantitative characteristics of specific interaction metallophthalocyanines with alcohol are obtained during the thermogravimetric study of metallophthalocyanine crystallsolvates with alcohol (Table 1). As it was mentioned earlier [8,10] the value of ΔH solvent from the corresponding crystalsolvate can be considered as an energy characteristics of specific interaction of metallophthalocyanines with solvent molecules as ΔH has two contributions, namely, the energy of breaking phthalocyanine–ethanol bonds and the work of exit when a substance passes into a gaseous state. The latter

Table 1
Physic-chemical characteristics of molecular complexes of aqueous-soluble metallophthalocyanines with alcohol

Metallophtphalocyanine	Complex	T_{dist}[c] (°C)	$\Delta_{evap}H$[b] (kJ mol^{-1})
Cu(4-COONa)$_4$Pc	1:4	90	34.42
Cu(3.5-COONa)$_8$Pc	1:4	45	39.88
Co(3-COONa)$_4$Pc	1:6	25	78.4
	1:1	54	30.4
Co(4-COONa)$_4$Pc	1:4	35	79.14
Zn(4-COONa)$_4$Pc[a]	1:4	70	86.7
Zn(3-COONa)$_4$Pc[a]	1:5	56	87.0
	1:1	76	106.0
Zn(4-SO$_3$Na)$_4$Pc	1:4	75	53.04
HOAl(4-COONa)$_4$Pc	1:6	30	28.46
	1:2	65	62.05

[a] Literature data [6].s
[b] $\Delta_{evap}H$ are calculated error is 0.8–1.5 kJ mol^{-1}.
[c] T_{dist}, distraction temperature.

contribution is insignificant and equals 2/3 kJ mol^{-1} [13]. Cu(4-COONa)$_4$Pc, Co(4-COONa)$_4$Pc, Zn(4-SO$_3$Na)$_4$Pc, Cu(3,5-COONa)$_8$Pc derivatograms are similar (Fig. 3). The process of ethanol evaporation from crystallsolvates of metallophthalocyanines mentioned above with alcohol proceeds in two stages. On the first stage $\Delta_{evap}H$ does not differ significantly from $\Delta_{evap}H$ of individual ethanol and shows that the solvate structures in which the ethanol interaction with metallophthalocyanines is presumably of a universal character are destroyed. On the second stage at higher temperatures and with $\Delta_{evap}H$ differing from $\Delta_{evap}H$ of pure ethanol the molecules of ethanol which specifically solvate metallophthalocyanine are evaporated from phthalocyanine crystalsolvate. Precise stoichiometry composition and high reproducibility of the results allow to come to conclusions that metallophthalocyanine complexes with ethanol by their nature are not the incorporation complexes. Simulteneous removal of four ethanol molecules from crystallsolvates of metallophthalocyanines with ethanol confirms specific solvation by ethanol molecules of four periphery phthalocyanine substituents. Derivatograms of HOA1(4-COONa)$_4$PC and Co(3-COONa)$_4$Pc crystallsolvates with ethanol are similar (Fig. 4). The evaporation process of a solvent from HOA1(4-COONa)$_4$PC and Co(3-COONa)$_4$Pc crystallsolvates with ethanol proceeds in many stages. The first stage is the destruction of solvate structures formed at the expense of van der Vaals interactions, then four ethanol molecules which are specifically solvat periphery metallophthalocyanine substituents are removed. In the third stage at higher temperatures specific HOAl(4-COONa)$_4$Pc·2EtOH, Co(3-COONa)$_4$PCEtOH complexes is destroyed. For Co(3-COONa)$_4$PC the coordination of an electron donating ethanol molecule in the sixth coordination place of Co^2 ion seems to occur. The higher coordination ability of cobalt ion in 3-carboxysubstituted phthalocyanine as compared with 4-carboxyderivative is probably due to the deformation of phthalocyanine macroring, which is caused by the presence of a substituent in the third position. The stability of Co^{2+}

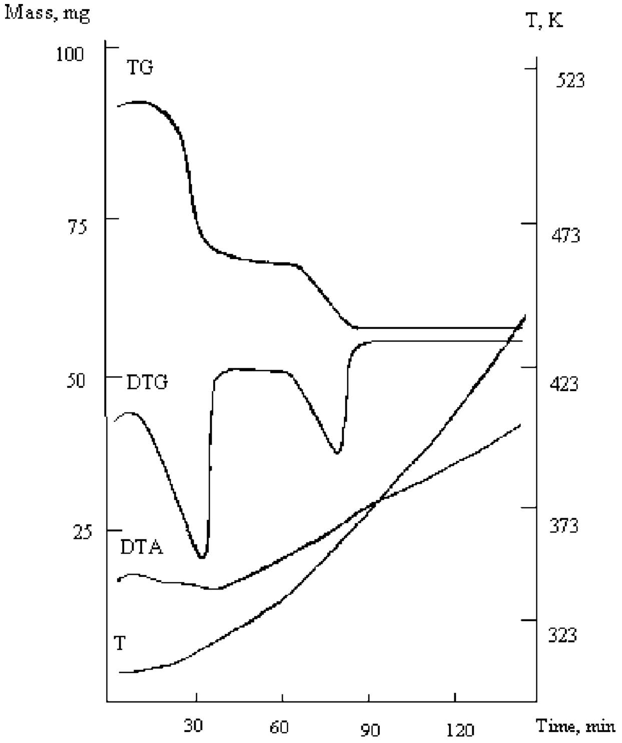

Fig. 3. Derivatograms of Cu(3,5-COONa)$_8$Pc crystalsolvate with ethanol. TG, thermogravimetry; DTG, differential thermogravimetry; DTA, differential thermal analyses; *T*, temperature.

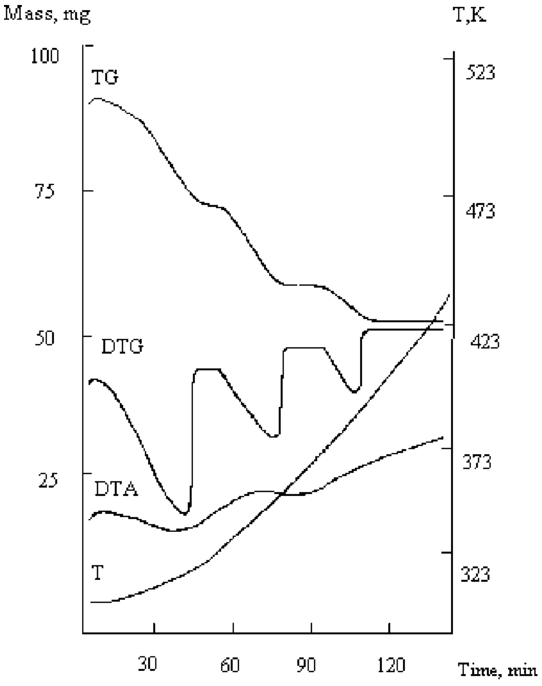

Fig. 4. Derivatograms of HOAl(4-COONa)$_4$Pc crystalsolvate with ethanol curves are given in Fig. 3.

with four nitrogen atoms of a reaction center σ-bonds of 3-carboxymetalphthalocianine decreases and the presence of a residual positive charge on cobalt ion helps the coordination of electron-donor molecules. Similar regularity was obtained earlier for metallophthalocyanines mentioned above with zinc(II). However, Zn(3-COONa)$_4$PC as well as Co(3-COONa)$_4$PC coordinates only one ethanol molecule. The comparison of energy characteristics of axial complexes of zinc(II)- and cobalt(II)-3-carboxyphthalocyanine with ethanol complexes testifies greater coordination ability of Zn^{2+} ion. Zinc ion forms four equivalent σ-bonds with phthalocyanine macrocycle. Stable electron $3d^{10}$ configuration seems not to form additional π-bonds. On the contrary, Co^{2+} ($3d^7$) ion in addition to four σ-bonds ($Co^{2+} \leftarrow N$) forms reverse donation π-bonds with phthalocyanine macrocycle ($Co^{2+} \rightarrow Pc_\pi$). The presence of similar π-donation interactions proves to decrease significantly the ability of a central metal ion to coordinate additional electron-donor molecules.

The composition of molecular HOAl(4-COONa)$_4$Pc complex proves to be rather sudden, two ethanol molecules being equally connected with a macrocycle. Relatively great radius of Al^{3+} triple charged ion and the presence of axial OH-ligand allow to stretch Al^{3+} ion out of a macrocycle plane, and due to it the coordination of ethanol in the 6th coordination site seems to be improbable. It is possible that in this case ethanol coordination on HOAl(4-COONa)$_4$Pc is being carried out at the expense of forming the hydrogen bonds between ethanol and axial OH-ligand of HOAl(4-COONa)$_4$Pc molecules. It is interesting to note that the energy stability of bonds between the molecules of ethanol and oxygen containing carboxy-4substituents of metallophthalocyanine is increased in the following series $Al^{3+} \leq Cu^{2+} < Co^{2+} < Zn^{2+}$. The dependence obtained confirms significant effect of the nature of a central metal ion on the coordination properties of carboxy–phthalocyanine groups. Energy characteristics of –COONa–EtOH hydrogen bond do not depend practically upon the position of a carboxyl substituent for one and the same phthalocyanine metallo-complex. Earlier while studying zinc(II)carboxyphthalocyanines [6] and zinc(II)porphyrines on the base of similar acid and complex forming properties of carboxy periphery macrocycle substituent it was concluded that in the composition of macro heterocyclic molecules the carboxyl groups possess similar physicochemical properties. The results obtained suggest that this conclusion is sometimes correct. In which way the central atom of phthalocyanine effects the main properties of periphery substituents. The induction effect does not differ greatly while passing from copper ion to cobalt and zinc. And it practically fully decays in three carbon–hydrogen bonds. The effect of a central metal ion on –COONa-groups in σ-bonds will be leveled. On the other hand metallophthalocyanine molecule is multi-contour. This fact confirms a very weak π-electron conjugation of benzene rings with eighteen central π-electrons of a macroring that is why the direct shift of electron density on π-bands which is due to π-donation interactions of a metal ion with a macroring does not seem to be possible. The data obtained (Table 1) and literature data [14,15] allow to suggest the fact that the mechanism of the influence of a central metal ion in a metallophthalocyanine molecule is more complicated than a conventional effect transfer on π or σ-bonds. For example Cu^{2+} and Co^{2+} metal ions forming with phthalocyanine reverse donation π-bonds while filling in the loosening π-orbitals of phthalocyanine increases their energy preventing $\pi \Leftrightarrow \sigma$ conversion of *n*-electrons of non-connecting nitrogen atom orbitals of a macroring. From metallophthalocyanines obtained the greatest tendency to form reverse donation π-bonds with a phthalocyanine macroring is displayed by copper ion. Al^{3+} ion possessing vacant p-orbitals forms the direct donation bonds with a phthalocyanine macrocycle. Thus, the formation of direct and reverse donation “metal ion–phthalocyanine” π-bonds results in redistribution of electron density on σ-bonds as well and is reflected on the coordination ability of periphery functional phthalocyanine substituents.

Physico-chemical characteristics of molecular complexes of water-soluble metallophthalocyanine with ethanol can be useful while analyzing the effect of alcohol additions on the state of metallophthalocyanines in solutions. Specific solvation of periphery substituents of metallophthalocyanines by alcohol molecules are certain to prevent π−π-dimerization of metallophthalocyanines studied, partially or completely shifting the equilibrium (1) towards the formation of monomers. The exception is Co(4-COONa)$_4$Pc which according to thermogravimetric analyses of its crystallsolvates with alcohol forms energetically stable complex with four ethanol molecules. Judging by the electronic absorption spectra of Co(4-COONa)$_4$Pc in water–ethanol solution the complex formation with four ethanol molecules does not influence the equilibrium (1). The fact allowed to suggest that in case of Co(4-COONa)$_4$Pc the aggregation of metallophthalocyanine molecules is carried out according to some other type but not π–π-interaction. The formation of Co(4-COONa)$_4$PC μ-oxo-dimers seems to take place, and the solvation of metallophthalocyanine by alcohol molecules on periphery does not have significant steric interference.

4. Conclusions

The results obtained indicate that the water-soluble metallophthalocyanines form molecular complexes with ethanol. It causes the shift of aggregation equilibrium to the formation of monomer form of the metallophthalocyanine.

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