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Aggregative Properties of Water-soluble Metal Phthalocyanines in a Borate Buffer Solution

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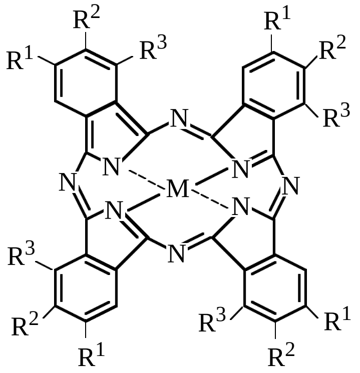
Abstract—Thermodynamic characteristics of dimerization of water-soluble zinc, copper, and cobalt complexes of sulfo- and carboxy-substituted phthalocyanines were obtained. A correlation of the aggregative capacity of the metal phthalocyanines with the nature of the central metal atoms and the number and position of peripheral substituents was revealed.

Metal complexes of carboxy- and sulfo-substituted phthalocyanines (MPc) have a high quantum yield of singlet oxygen, which makes them perspective catalysts and photosensors. However, the fact that these MPc exhibit tendency for aggregation in aqueous media prevents their wide practical application. Association and aggregation of macrorings, including carboxy-substituted MPc, in solutions have been fairly well studied by electronic spectroscopy [1–9]. Analysis of the reported thermodynamic results revealed a number of problems associated with the applicability of electronic spectroscopy for studying MPc in solutions. First, this method works if MPc are photostable at least over the course of spectral measurements. Even though up to now there has been no information of photostability of carboxyphthalocianines, their dimerization constants have been determined by means of electronic spectroscopy [10, 11]. However, as shown [12, 13], carboxy-substituted MPc are not all photostable {for example, zinc(II) octacarboxyphthalocyanine decomposes by 50% within 3 min under irradiation with a quartz lamp (220 W, light filter λ 600 nm [12, 13]}. This evidence obviously lessens the value of the results in [10, 11]. Second, the number of various aggregate forms of MPc present in the solution is impossible to estimate from the absorption intensity in the electronic spectrum, since, for example, the absorption bands of MPc monomers and dimers overlap [1–9], and those of dimers and trimers overlap by more than 90% [14]. The extinctions of the monomers and dimers are calculated under various assumptions. For example, assuming that infinitely dilute solutions contain the monomeric forms exclusively [5–9, 15, 16], the ε_m values determined in detergent solutions are used for strongly aggregating compounds [5–9, 15, 17, 18]. Still more oversimplified assumptions are used when the ε values are determined by shifting equilibrium (1) to dimer formation by, for example, adding a salt and increasing macroheteroring concentration in the solution; therewith, higher aggregates, as well as the dependence of ε on ionic strength are neglected. With MPc, spectral studies are complicated by the ability of these compounds to be absorbed on glass surfaces [19]. Third, electronic spectroscopy cannot provide all required thermodynamic characteristics of MPc with charged peripheral substituents, since increasing temperature decreases the ionization degree of phthalocyanine substituents and, consequently, changes the state of MPc in solutions. Therefore, K not always linearly varies with temperature, which makes ΔH difficult to determine by the van't Hoff's equation.

Probably, the fact that the ΔK values obtained by different authors for the same systems vary several orders of magnitude points to illegitimacy of the above-mentioned assumptions and makes the aggregative ability of various MPc impossible to compare and discuss [1–19]. We could find a single work in the literature, where thermodynamic characteristics of process (1) for sulfo-substituted copper(II) phthalocyanine [20] have been determined by calorimetric and spectral methods [21]. The resulting data astonishingly well fit each other. Critical analysis of the calorimetric experiment in [20] revealed a number of methodical errors that might give rise to such results. In the referred calorimetric experiment, a 0.01 M solution of sulfo-substituted copper(II) phthalocyanine was used as initial on the assumption that such a supersaturated solution of MPc contains no higher aggregates. Even at superficial glance [1–19] such assumptions seem to be untrue. The aim of the present work was to study the aggregation properties of water-soluble MPc with various positions, number, and nature of peripheral substituents. As objects for study we chose zinc complexes of tetra-4-carboxyphthalocyanine [Zn(4-$CO_2H)_4$Pc], tetra-3-carboxyphthalocyanine [Zn(3-$CO_2H)_4$Pc], octa-4,5-carboxyphthalocyanine [Zn(4,5-$CO_2H)_8$Pc], and tetra-4-sulfophthalocyanine [Zn(4-$SO_3H)_4$Pc], copper complexes of tetra-4-carboxyphthalocyanine [Cu(4-$CO_2H)_4$Pc] and octa-3,5-carboxyphthalocyanine [Cu(3,5-$CO_2H)_8$Pc], and cobalt complexes of tetra-3-carboxyphthalocyanine [Co(3-$CO_2H)_4$Pc], tetra-4-carboxyphthalocyanine [Co(4-$CO_2H)_4$Pc], and tetra-4-sulfophthalocyanine [Co(4-$SO_3H)_4$Pc].



M = Zn, $R^1 = R^3$ = H, $R^2 = CO_2H$; $R^1 = R^2$ = H, $R^3 = CO_2H$; $R^1 = R^2 = CO_2H$, R^3 = H; $R^1 = R^3$ = H, $R^2 = SO_3H$. M = Cu, $R^1 = R^2 = =$ H, $R^3 = CO_2H$; $R^1 = R^3 = CO_2H$, R^2 = H. M = Co, $R^1 = CO_2H$, $R^2 = R^3$ = H; $R^1 = R^3$ = H, $R^2 = CO_2H$; $R^1 = R^3$ = H, $R^2 = SO_3H$.

Dissolution of MPc in aqueous alkaline solutions occurs via salt formation.

The thermodynamic characteristics were calculated by Eqs. (1) and (2) from the results of calorimetric titration of MPc solutions with pyridine.

$$(\mathrm{MPc})_2 \overset{K_1}{\rightleftarrows} \mathrm{MPc} + \mathrm{MPc}, \qquad (1)$$

$$\mathrm{MPc} + \mathrm{L} \overset{K_2}{\rightleftarrows} \mathrm{MPc\cdot L}. \qquad (2)$$

The equilibrium constants of the first (K_1) and second (K_2) stages of the process are given by Eqs. (3) and (4).

$$K_1 = [\mathrm{MPc}]_n^2/[(\mathrm{MPc})_2]_n$$
$$= [\mathrm{MPc}]_n^2/(c^0_{(\mathrm{MPc})_2})_n - 1/2[\mathrm{MPc}]_n - 1/2[\mathrm{MPc\cdot L}]_n, \qquad (3)$$
$$K_2 = [\mathrm{MPc\cdot L}]_n/[\mathrm{MPc}]_n[\mathrm{L}]_n$$
$$= [\mathrm{MPc\cdot L}]_n/[\mathrm{MPc}]_n\{(c^0_{\mathrm{L}})_n - [\mathrm{MPc\cdot L}]_n\}. \qquad (4)$$

Via a series of transformations we obtain the final expression (5).

$$[\mathrm{MPc}]_n^3 + [\mathrm{MPc}]_n^2(1/K_2 + K_1/2) + [\mathrm{MPc}]_n[K_1/2K_2 + (K_1/2)(c^0_{\mathrm{L}})_n - K_1(c^0_{(\mathrm{MPc})_2})_n] = K_1/K_2(c^0_{(\mathrm{MPc})_2})_n. \qquad (5)$$

Here $[\mathrm{MPc\cdot L}]_n$, $[\mathrm{MPc}]_n$, $[(\mathrm{MPc})_2]_n$, and $[\mathrm{L}]_n$ are the equilibrium concentrations of the molecular complex, MPc, dimeric MPc, and pyridine, respectively; $(c^0_{(\mathrm{MPc})_2})_n$ and $(c^0_{\mathrm{L}})_n$, initial concentrations of MPc and pyridine, respectively, after addition of the *n*th portion of the titrant; and *n*, titration step.

The quantity of heat evolved on addition of the *n*th portion of the titrant (Q_n) was calculated by Eq. (6).

$$Q_n = -(\Delta H_1 V_n[\mathrm{MPc}]_n + \Delta H_2 V_n[\mathrm{MPc\cdot L}]_n). \qquad (6)$$

Here V_n is the volume of the reaction mixture.

The K_1, K_2, ΔH_1, and ΔH_2 values were determined by coordinate descent optimization combined with least-squares treatment. The set of Eqs. (1) and (2) in each step of the optimization procedure was solved using the Maple 8 program package. The equilibrium concentrations [MPc] and [MPc · L] were substituted into Eq. (6), and the numerical values of ΔH_1 and ΔH_2 were calculated by a simple linear regression. The optimization process was terminated when a minimum of the $\Sigma[Q_n(\mathrm{exp}) - Q_n(\mathrm{cal})]^2$ function was reached.

Any descent method fails on an unordered relief. If there are many local extrema, then descent from one approximation can converge to only one local minimum. This minimum is not necessarily global; the global minimum was found by random search [22]. It is suggested that the minimum of interest locates in a certain closed region. A few points are taken (usually 10–15 pairs of random K_1 and K_2 values), and a descent is made from each point. By comparing (visually or by means of a program) final values of the $\Sigma[Q_n(\mathrm{exp}) - Q_n(\mathrm{cal})]^2$ function one select minima appropriate in terms of the research task, and further descents are made from these points to obtain minimum constants and constants to a high accuracy.

The fact that the thermodynamic characteristics of the processes are independent of MPc concentration provides evidence for the suggestion that in the concentration region studied (10^{-7}–10^{-6} M) there exist primarily monomeric and dimeric forms of MPc. Further control of the variation of the degree of MPc aggregation [schemes (1) and (2)] was accomplished using the electronic absorption spectra.

The resulting thermodynamic characteristics of the MPc dimerization process (see table) cannot, strictly

Thermodynamic characteristics of MPc dimerization in a borate buffer solution at 298.15 K

MPc	K_1	$-\Delta H_1$, kJ mol^{-1}	$-\Delta S_1$, J mol^{-1} K^{-1}
Zn(4-CO_2Na)$_4$Pc	$6.8 \times 10^5 \pm 4.5 \times 10^3$	102.97 ± 0.06	234 ± 16
Zn(3-CO_2Na)$_4$Pc	$2.96 \times 10^4 \pm 1.4 \times 10^2$	79.86 ± 0.04	182 ± 22
Zn(4,5-CO_2Na)$_8$Pc	$1.56 \times 10^{-3} \pm 3.5 \times 10 \pm 5$	57.68 ± 0.08	247 ± 21
Zn(4-SO_3Na)$_4$Pc	$4.18 \times 10^4 \pm 6.7 \times 10^2$	131.07 ± 0.06	351 ± 17
Co(4-CO_2Na)$_4$Pc	$2.96 \times 10^5 \pm 5.1 \times 10^3$	66.45 ± 0.07	118 ± 14
Co(3-CO_2Na)$_4$Pc	$3.09 \times 10^3 \pm 15$	61.52 ± 0.03	140 ± 19
Co(4-SO_3Na)$_4$Pc	$9.26 \times 10^3 \pm 13$	101.67 ± 0.02	265 ± 20
Cu(4-CO_2Na)$_4$Pc	$1.06 \times 10^{11} \pm 9.8 \times 10^9$	146.23 ± 0.09	279 ± 18
Cu(3,5-CO_2Na)$_8$Pc	$7.52 \times 10^3 \pm 64$	94.80 ± 0.05	244 ± 12

speaking, be considered standard, since they were determined at a strictly defined ionic strength ($I \sim 0.1$). However, the thermodynamic characteristics obtained under the same experimental conditions still allow one to assess the effect of various factors on the tendency of MPc for dimerization.

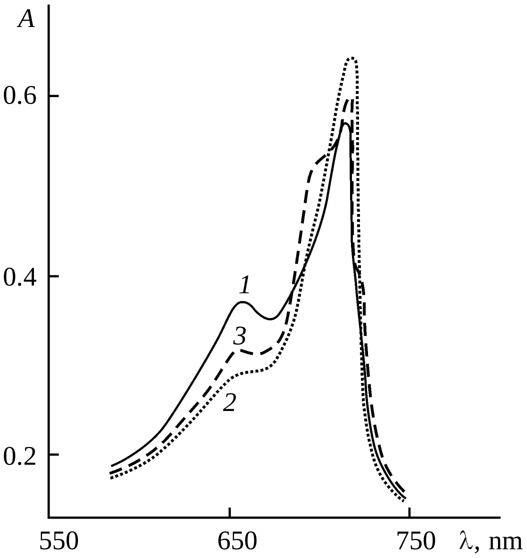
The tendency of zinc(II) phthalocyanines for dimerization (see table) increases in the order Zn(4,5-CO_2Na)$_8$Pc < Zn(3-CO_2Na)$_4$Pc < Zn(4-SO_3Na)$_4$Pc < Zn(4-CO_2Na)$_4$Pc. According to [10, 11, 23], the sulfo- and carboxy-substituted zinc(II) phthalocyanines in hand dimerize in aqueous solutions by the π–π type. The dimerization involves π–π interaction between the aromatic systems of the macrosyslic molecules and is controlled by electrostatic repulsion between negatively charged peripheral substituents. The resulting data suggest increasing number pf negatively charged substituents is the most effective impediment to dimerization of zinc(II) phthalocyanines. The weaker tendency of Zn(3-CO_2Na)$_4$Pc for dimerization compared with Zn(4-CO_2Na)$_4$Pc is probably associated with steric hindrances from the 3-COOH substituent, as in this case the Zn(3-CO_2Na)$_4$Pc molecule is nonplanar.

Note that dimerization of carboxy-substituted zinc(II) phthalocyanines involves strong heat release, the energy gain of the process increasing in the order Zn(4,5-CO_2Na)$_8$ < Zn(3-CO_2Na)$_4$Pc < Zn(4-CO_2Na)$_4$ · Pc. This result makes us to state that this process is enthalpy-controlled. The dimerization constant of Zn(4-SO_3Na)$_4$Pc is 16-fold lower than K_1 for Zn(4-CO_2Na)$_4$Pc, but, therewith, the former dimerizes more exothermally that the latter.

The stronger tendency of carboxyphthalocyanines for aggregation in aqueous media, as compared to their sulfo analogs, have been repeatedly mentioned in the communications concerning the electronic absorption spectra of MPc [24, 25]. The lack of direct correlation between K_1 and ΔH in dimerization of Zn(4-SO_3Na)Pc and Zn(4-CO_2Na)$_4$Pc, revealed in the present work, may be related exclusively to an effect of peripheral functional substituents. The four SO_3Na substituents whose van der Waals radius is ~1.4 that of CO_2Na [26] hinder π–π interaction between the aromatic systems of the two phthalocyanine molecules in the dimeric structure, and. therefore, the Zn(4-SO_3Na)$_4$Pc dimer is thermodynamically less stable than the Zn(4-CO_2Na)$_4$Pc dimer. On the other hand, the sulfo group is less prone to hydrogen bonding with protic solvents than COOH [23]. Probably, the more exothermic dimerization of Zn(4-SO_3Na)$_4$Pc compared with Zn(4-CO_2Na)$_4$Pc is explained by lower energy expenditures for the dehydration of peripheral substituents in Zn(4-SO_3Na)$_4$Pc, that precedes dimerization.

Mechanistically, carboxy-substituted copper(II) phthalocyanine complexes, like their zinc(II) analogs, dimerize by the π–π type. As seen from the table, the aggregative ability of Cu(4-CO_2Na)$_4$Pc is stronger than that of Cu(3,5-CO_2Na)$_8$Pc by 7 orders of magnitude. Probably, the much weaker tendency of Cu(3,5-CO_2Na)$_8$Pc for aggregation is explained by a cooperative effect, namely, the steric hindrances created by the bulky 3-COOH substituents and the stronger electrostatic repulsion between 8 likely charged substituents compared with 4 such substituents in Cu(4-CO_2Na)$_4$Pc.

From a comparison of the thermodynamic characteristics of copper(II) and zinc(II) tetra-4-carboxyphthalocyanines it follows that the central atom exerts a strong effect on the aggregation process. The role of the central metal atom in formation of π–π dimers and/or π–π complexes of macroheterocycles with aromatic compounds is still an open question. Some evidence is available showing that introduction of a metal has no effect on the geometry of π–π complexes but favors enhanced interaction between two aromatic



Electronic absorption spectrum of Co(4-$SO_3Na)_4$Pc (*c* 5.45×10^{-6} M) in a borate buffer solution (pH 9.65) (*1*) immediately after preparation, (*2*) after 2 h, and (*3*) on addition of pyridine.

molecules [27–29]. Shelnutt [27] in a thermodynamic study on the π–π interaction of metal complexes of watersoluble porphyrins with phenanthroline came to a conclusion that, as the Gibbs energy is almost independent on the nature of the metal, the latter is not directly involved in π–π interaction. Tnerewith, the referee did not rule out involvement of the pz orbitals of the metal atom in complex formation. Chamaeva and Kitaigorodskii [30], by contrast, interpreted their results on formation of π–π complexes in which aromatic nitro compounds locate over the metal ion in terms of direct involvement of the latter in intermolecular π–π interaction. What is the mechanism of the effect of the central metal atom on MPc dimerization? Relying on the theory of π–π interactions, proposed by Hunter and Sanders [29], the role of a metal ion bearing residual positive charge is limited by electrostatic interaction with the negatively charged electronic cloud of the second phthalocyanine molecule. However, this reasoning is unlikely to explain the fact that the dimerization constants of Cu(4-$CO_2Na)_4$Pc and Zn(4-$CO_2Na)_4$Pc differ from each other more than 105 times. Moreover, Cu^{2+} ($3d^9$), unlike Zn^{2+} ($3d^{10}$) that forms four σ bonds (M←N), with the phthalocyanine macroring, is capable for additional π-dative interactions ($M \rightarrow \pi_N$), as a result of which the residual positive charge on the copper(II) ion is neutralized to a greater extent than on the zinc(II) ion. These results suggest that the theory proposed in [29] fails to fit the experimental data, and π–π dimerization of such complex molecules as phthalocyanines cannot be considered in terms of electrostatic interaction of point charges (π–σ attraction and π–π repulsion). Introduction of a metal into a phthalocyanine molecule produces electron density redistribution, which is especially relates to metals capable for back π-dative interactions ($M \rightarrow \pi_N$). Therewith, metal d_π orbitals interact with phthalocyanine antibonding π orbitals, thus increasing the energy of the latter [31] and preventing *n* orbitals of *meso*-nitrogen atoms from π conjugation. Such a strong dependence of the MPc dimerization process on the state of the aromatic system allows this reaction to be considered as a donor–acceptor interaction between two aromatic systems.

Cobalt(II) phthalocyanines occupy a special place among the MPc studied. The peculiarity of these macroheterocycles consists in that they can form different dimers in aqueous media, depending on conditions. Moreover, cobalt(II) phthalocyanines tend to form stable molecular complexes with O_2 [32, 33]. When measuring the electronic absorption spectra of borate solutions of Co(4-$SO_3Na)_4$Pc before calorimetric experiments, we detected relaxation effects (see figure). Usually [34] relaxation effects reflect changes associated with the aggregation state. However, the detected enhancement of the *Q* band cannot be related to Co(4-$SO_3Na)_4$Pc dimerization or aggregation. In the electronic absorption spectra measured after calorimetric titration, a much attenuated absorption of the Co(4-$SO_3Na)_4$Pc solution at λ 620 nm and splitting of the *Q* band into two components are observed (see figure).

By examining spectral data for Co(4-$SO_3Na)_4$Pc we revealed controversial interpretations of the electronic absorption spectra of aqueous solutions of Co(4-$SO_3Na)_4$Pc. Thus, Abel *et al.* [35] associate the relaxation effect that manifests itself in the long-wave shift of the *Q* band and its enhancement with the oxidative process Co(II) > Co(III). However, we consider more convincing the arguments of Cruen and Blagrove [36] who explain the above spectral changes by formation of a molecular complex between Co(4-$SO_3Na)_4$Pc and O_2 that is always present in aqueous solutions (see figure). Probably, this is the reason why the tendency of Co(4-$SO_3Na)_4$Pc for dimerization is stronger 4.5 times than that of Zn(4-$SO_3Na)_4$Pc. Coordination of Co(4-$SO_3Na)_4$Pc occurs more exothermally that dimerization of carboxy-substituted cobalt(II) phthalocyanines, and the obtained Δ*H* values compare with the Δ*H* of Zn(4-$SO_3Na)_4$Pc dimerization. The absence from the electronic absorption spectra of Co(4-$SO_3Na)_4$Pc of the absorption maximum at λ 610–616 nm, corresponding to the Co(4-$SO_3Na)_4$Pc dimer comprising 12 water molecules and the similarity of the thermodynamic patterns of $Co(4-SO_3Na)_4Pc$ and $Zn(4-SO_3Na)_4Pc$ dimerization suggest a π–π type of $Co(4-SO_3Na)_4Pc$ dimerization in the borate buffer solution. By contrast, as follows from our previous results, dimerization of $Co(3-CO_2Na)_4Pc$ in aqueous alkaline solutions occurs via formation of an oxygen bridge that links the cobalt(II) ions of two phthalocyanine molecules, i.e. a μ-oxo dimer is formed. The dimerization enthalpies of $Co(3-CO_2Na)_4Pc$ and $Co(4-CO_2Na)_4Pc$ compare with each other; therewith, $Co(4-CO_2Na)_4Pc$ exhibits a stronger tendency for dimerization than $Co(3-COONa)_4Pc$. If in borate buffer solutions $Co(3-COONa)_4Pc$, too, forms μ-oxo dimers, then the observed differences (see table) suggest different mechanisms of the effects of the *para* and *ortho* substituents in $Co(4-CO_2Na)_4Pc$ and $Co(3-CO_2Na)_4Pc$, respectively. The 4-COOH substituent in the phthalocyanine macroring effectively transmits the negative polar effect [37], thus decreasing the electron density of the nitrogen atoms of the phthalocyanine reaction center and finally enhancing the coordinative ability of Co^{2+}. The resulting data (see table) establish that the effect of the 4-COOH group on the coordinative ability of the central metal ion toward electron-donor molecules is stronger than the polar effect of the 3-COOH group and the steric distortion of the phthalocyanine macroring, produced by this group.

Thus, our study showed that both μ-oxo and π–π dimerization of metal phthalocyanines are enthalpy-controlled processes. In the latter case, increasing number of likely charged substituents adversely affects the tendency of the macroring for aggregation in solutions. Carboxy-substituted MPc exhibit a stronger tendency for aggregation in borate buffer solutions than their sulfo analogs. The tendency of the MPc studied for dimerization decreases in the order $Cu(4-CO_2Na)_4Pc > Zn(4-CO_2Na)_4Pc > Co(4-CO_2Na)_4Pc > Zn(4-SO_3Na)_4Pc > Zn(3-CO_2Na)_4Pc > Co(4-SO_3Na)_4Pc > Cu(3.5-CO_2Na)_8Pc > Co(3-CO_2Na)_4Pc > Zn(4,5-CO_2Na)_8Pc$.

EXPERIMENTAL

The carboxy-substituted MPc were synthesized and purified according to [38]. Crystalline samples were subjected to a vacuum at 343–353 K to constant weight to remove solvent molecules. The purity of the resulting samples was controlled by the electronic absorption spectra in DMF, measured on a Specord M-40 spectrophotometer.

Calorimetry was performed in a borate buffer (pH 9.65) using a highly sensitive differential automated titration calorimeter [39].

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