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Aggregation properties of water-soluble metal phthalocyanines: effect of ionic strength of solution

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Standard thermodynamic characteristics of dissociation (dimerization) of sulfo- and carboxysubstituted metal phthalocyanines were determined for the first time by calorimetric titration. The influence of the nature, number, and position of peripheral substituents of the macrocycle, the electronic structure of the central metal ion, and the ionic strength of solution on the thermodynamic stability of the phthalocyanine dimers was estimated.

Key words: metal phthalocyanines, dimerization, thermodynamics, calorimetry of titration.

The use of metal phthalocyanines (MPc) as sensors in photodynamic therapy of oncological diseases is based on the ability of their molecules to be photoexcited to the triplet state and interact with oxygen, transforming the latter into its excited singlet state.[1,2] Metal phthalocyanines are better photosensitizers in diagnostics and therapy of malignant neoplasms than metal porphyrins, because they absorb intensely in the long-wave region of the visible spectrum (in the so-called "therapeutic window," at wavelengths > 600 nm). Therefore, photosensors of the second generation are based on phthalocyanines. The photoactivity of MPc is directly related to their state in solutions.[3—5] Photoinduced processes accompanying the formation of MPc dimers includes bimolecular triplet annihilation, due to which the excited triplet state decays, the quantum yield of $^1O_2$ ($^1\Delta_g$) decreases,[6—10] and, thus, dimerization manifold decreases the photoactivity of MPc.[6—8] The influence of electrolytes on the affinity to dimerization of macroheterocyclic molecules with peripheral charged substituents were multiply described at a qualitative level.[5,8—11] Anion-cationic interactions affect substantially the aggregation state of MPc and also can determine the efficiency of MPc through binding with biological substrates. For instance, the interaction of sulfosubstituted derivatives of MPc with albumin, which is the main protein of the blood plasma, is predominantly electrostatic[12] and, hence, water-soluble MPc can be administrated intravenously without "external" active transport agents. According to published data,[12] albumin with a high affinity to negatively charged molecules can act as the main endogenic mediator, in particular, for sulfosubstituted derivatives of MPc, and determine the distribution of photosensor molecules over the circulatory system in the organism. A possibility to use MPc as inactivators of bacteria and viruses is another practically important aspect that makes research of the anion-cationic interactions of MPc with biological substrates to be a study of challenge. Despite the evident significance, quantitative studies of the aggregation properties of MPc in aqueous media are scarce because of methodological and experimental difficulties.

The purpose of this work is to study the aggregation of a wide series of sulfo- and carboxysubstituted MPc derivatives in borate buffer solutions by calorimetric titration, determine the standard thermodynamic characteristics of dissociation of the metal phthalocyanine dimers, and estimate the influence of the number and position of substituents in the macrocycle on the dimerization affinity of the corresponding MPc. An important part of the study is aimed at revealing the effect of the ionic strength of solution on the thermodynamic characteristics of the dissociation of the metal phthalocyanine dimers. The phthalocyanine complexes with ions Zn^{2+}, Cu^{2+}, Co^{2+}, and Al^{3+} were chosen to estimate the effect of the nature of the central metal atom in the dimerization affinity of the corresponding MPc.

Experimental

Tetra-4-carboxyphthalocyaninealuminum(III) HOAl(4-COOH)$_4$Pc, tetra-4-carboxyphthalocyaninecopper(II) Cu(4-COOH)$_4$Pc, tetra-4-carboxyphthalocyaninecobalt(II) Co(4-COOH)$_4$Pc, tetra-4-carboxyphthalocyaninezinc(II) Zn(4-COOH)$_4$Pc, tetra-4-sulfophthalocyaninezinc(II) Zn(4-SO$_3$H)$_4$Pc, tetra-4-sulfophthalocyaninecobalt(II) Co(4-SO$_3$H)$_4$Pc, tetra-3-carboxyphthalocyaninezinc(II) Zn(3-COOH)$_4$Pc, tetra-3-carboxyphthalocyaninecobalt(II) Co(3-COOH)$_4$Pc, octa-3,5-carboxyphthalocyaninecopper(II) Cu(3,5-COOH)$_8$Pc, and octa-4,5-carboxyphthalocyanine-

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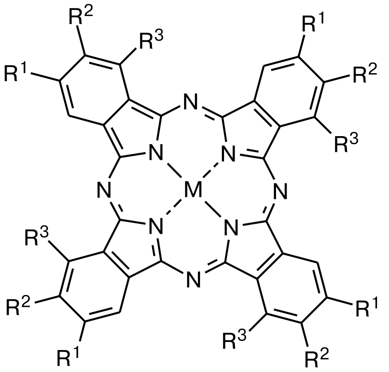
zinc(II) $Zn(4,5\text{-}COOH)_8Pc$ were synthesized and purified by standard procedures.[13]



M = Al(OH), $R^1 = R^3 = H$, $R^2 = COOH$;
M = Cu, $R^1 = R^3 = H$, $R^2 = COOH$;
M = Co, $R^1 = R^3 = H$, $R^2 = COOH$;
M = Zn, $R^1 = R^3 = H$, $R^2 = COOH$;
M = Zn, $R^1 = R^3 = H$, $R^2 = SO_3H$;
M = Co, $R^1 = R^3 = H$, $R^2 = SO_3H$;
M = Zn, $R^1 = R^2 = H$, $R^3 = COOH$;
M = Co, $R^1 = R^2 = H$, $R^3 = COOH$;
M = Cu, $R^2 = H$, $R^1 = R^3 = COOH$;
M = Zn, $R^1 = R^2 = COOH$, $R^3 = H$.

Crystalline samples were dried to a constant weight *in vacuo* at 343—353 K to remove solvent molecules. The purity of the synthesized substances was monitored by the electronic absorption spectra (EAS) of MPc in DMF and DMSO, which showed a good coincidence with the published data.[13]

Calorimetric studies were carried out in a borate buffer (74 mL of a solution of borax (19.1 g $Na_2B_4O_7 \cdot 10H_2O$ per 1000 mL of H_2O) and 26 mL of 0.1 *M* NaOH) at pH 9.65 using a high-sensitivity differential calorimeter for titration.[14] The MPc under study are dissolved in borate buffer solutions due to the formation of the corresponding sodium salts.

The ionic strength of phthalocyanine-containing solutions was created by sodium chloride; NaCl (reagent grade) was purified by recrystallization from water and dried *in vacuo* at 380—390 K. Twice-distilled deionized water was used to prepare solutions. To determine thermal effects of dissolution of phthalocyanine solutions, a solution of NaCl in a borate buffer was placed in a feeder, and cell was filled with a solution of MPc (10^{-7}—10^{-6} mol L^{-1}) in a borate buffer with NaCl. For a blank experiment, both the calorimetric cell and feeder were filled with a solution of NaCl in a borate buffer. The blank experiment made it possible to take into account the thermal effects related to the introduction of a titrant and a change in the thermal capacity of the solution in the cell. A change in the degree of MPc aggregation after experiment was additionally monitored from the electronic absorption spectra of MPc on a Specord M-40 spectrophotometer.

To characterize the thermodynamic characteristics (K, ΔH) of the process

$$(MPc^{n-}Na^+{}_n)_2 \xrightleftharpoons{K} MPc^{n-}Na^+{}_n + MPc^{n-}Na^+{}_n \qquad (1)$$

(n is the number of peripheral substituents in MPc) by the results of the calorimetric experiment, the following procedure was used.

1. At each chosen value of K_i (K_i is specified from 0 to $+\infty$, i is the number of iterations), we calculated x_0 as the equilibrium concentration of MPc in the monomeric form before the first dose was introduced

$$x_0 = 0.25\sqrt{K_i^2 + 8K_iC_0} - K_i.$$

2. Taking into account dilution upon dosing, the MPc concentration in a calorimetric cell is

$$C_{01} = C_0V_0/(V_0 + V_d),$$

where V_0 is the initial volume of a solution in the cell, and V_d is the dose volume.

3. At each chosen array of K_i and C_{01} values, we calculated the equilibrium concentration of MPc in the monomeric form (x_1) after the first dose was added.

4. Amounts of MPc before (ν_0) and after (ν_1) dosing and the increment of the MPc amount ($\Delta\nu$) were determined by the formulas

$$\nu_0 = x\nu_0,$$
$$\nu_1 = x_1(V_0 + V_d),$$
$$\Delta\nu = \nu_1 - \nu_0.$$

5. Thermal effect of the process is

$$\Delta H_1 = Q_1/\Delta\nu = Q_1/[x_1(V_0 + V_d) - xV_0],$$

where Q_i is the unity thermal effect, which was preliminarily corrected taking into account the corresponding unity thermal effect of the blank experiment.

6. At the same K_i, the calculations were performed for the second dose. The concentration was recalculated taking into account dilution

$$C_{02} = C_0V_0/(V_0 + 2V_d).$$

7. For each chosen array of K_i and C_{02} values, we calculated the equilibrium concentration x_2 after the second dose was introduced.

8. Amount of MPc (ν_2) after the second dose was introduced is

$$\nu_2 = x_2(V_0 + 2V_d).$$

9. Increment of the amount of MPc in the monomeric form was determined as

$$\Delta\nu = \nu_2 - \nu_1.$$

10. Thermal effect of the process is

$$\Delta H_2 = Q_2/[x_2(V_0 + 2V_d) - x_1(V_0 + V_d)].$$

The calculations gave an array of values ΔH_1, ΔH_2, ΔH_3, ..., ΔH_n, and the mean-root-square deviation and adequacy dispersion were calculated as

$$S^2 = [\sum_{i=1}^{n}(\Delta H_{av} - \Delta H_i)]/(n-1).$$

The Newton—Rafson optimization method[15] was used to minimize S^2.

The change in the entropy of the process under study (ΔS) was calculated by the equation

$$\Delta S = (\Delta H + RT\ln K)/T,$$

where R is the universal gas constant.

The error of determination of the thermodynamic characteristics was calculated according to traditional procedures.[15,16]

Results and Discussion

In this work, calorimetric titration was used for the first time to study MPc dimerization. This method made it possible to obtain the thermodynamic characteristics of dissociation of the dimeric phthalocyanine molecules (Table 1). It follows from the results of previous stud-

Table 1. Thermodynamic characteristics[a] of the dissociation of the MPc dimers in a borate buffer solution at different ionic strengths of the medium

MPc	I	ΔH^b	K	ΔS^c
$Zn(4\text{-}COONa)_4Pc$	0.12	88.009	$3.53\cdot10^{-8}$	153
	0.37	104.801	$2.60\cdot10^{-8}$	206
	0.43	108.004	$2.47\cdot10^{-8}$	217
	0.51	115.207	$2.13\cdot10^{-8}$	240
	0.62	124.800	$1.66\cdot10^{-8}$	270
	0.69	131.642	$1.43\cdot10^{-8}$	291
	0.77	138.412	$1.14\cdot10^{-8}$	312
	0.89	142.409	$7.20\cdot10^{-9}$	322
	0.90	150.094	$7.10\cdot10^{-9}$	347
	1.03	159.027	$2.72\cdot10^{-9}$	369
	1.09	160.861	$9.56\cdot10^{-10}$	367
$Zn(4\text{-}SO_3Na)_4Pc$	0.12	113.925	$1.13\cdot10^{-6}$	268
	0.39	122.979	$7.03\cdot10^{-7}$	295
	0.428	132.295	$6.32\cdot10^{-7}$	325
	0.502	140.308	$5.12\cdot10^{-7}$	350
	0.515	143.274	$5.35\cdot10^{-7}$	360
	0.578	152.273	$4.16\cdot10^{-7}$	389
	0.647	157.481	$2.93\cdot10^{-7}$	403
	0.671	158.044	$2.64\cdot10^{-7}$	404
$Zn(3\text{-}COONa)_4Pc$	0.12	70.432	$1.73\cdot10^{-6}$	126
	0.39	72.284	$1.33\cdot10^{-6}$	130
	0.43	73.069	$1.27\cdot10^{-6}$	132
	0.48	74.145	$1.20\cdot10^{-6}$	135
	0.502	74.711	$1.14\cdot10^{-6}$	137
	0.578	77.659	$9.60\cdot10^{-7}$	145
	0.653	81.766	$8.01\cdot10^{-7}$	158
$Zn(4,5\text{-}COONa)_8Pc$	0.12	42.286	178	185
	0.37	73.550	131	287
	0.451	89.751	128	341
	0.555	104.000	64	383
	0.647	123.415	0.1004	395
	0.693	130.897	0.0132	403
	0.74	141.729	0.0027	426
$Cu(4\text{-}COONa)_4Pc$	0.12	142.226	$8.71\cdot10^{-9}$	323
	0.417	174.094	$3.88\cdot10^{-9}$	423
	0.428	172.342	$3.86\cdot10^{-9}$	417
	0.476	195.684	$3.14\cdot10^{-9}$	494
	0.493	195.356	$3.04\cdot10^{-9}$	492
	0.578	205.852	$1.37\cdot10^{-9}$	521
$Cu(3,5\text{-}COONa)_8Pc$	0.12	91.935	$1.34\cdot10^{-4}$	234
	0.424	96.367	$1.11\cdot10^{-4}$	248
	0.52	97.675	$9.89\cdot10^{-5}$	251
	0.578	98.02	$9.43\cdot10^{-5}$	252
	0.647	99.305	$8.82\cdot10^{-5}$	255
	0.699	99.979	$8.43\cdot10^{-5}$	257
	0.878	101.081	$6.44\cdot10^{-5}$	259
	0.903	101.96	$6.32\cdot10^{-5}$	262
	1.034	104.012	$4.03\cdot10^{-5}$	265
	1.103	105.816	$1.08\cdot10^{-5}$	260
$OHAl(4\text{-}COONa)_4Pc$	0.12	61.999	$7.00\cdot10^{-5}$	128
	0.359	66.001	$6.37\cdot10^{-5}$	141
	0.427	67.493	$6.12\cdot10^{-5}$	146
	0.47	68.439	$5.95\cdot10^{-5}$	149
	0.514	68.910	$5.73\cdot10^{-5}$	150
	0.593	69.333	$5.33\cdot10^{-5}$	151
	0.82	70.460	$3.54\cdot10^{-5}$	151
	0.878	73.810	$2.93\cdot10^{-5}$	161
	1.03	81.899	$3.13\cdot10^{-5}$	188
$Co(4\text{-}COONa)_4Pc$	0.106	53.191	$8.37\cdot10^{-7}$	62
	0.36	58.102	$6.86\cdot10^{-7}$	77
	0.44	60.594	$6.24\cdot10^{-7}$	84
	0.473	62.344	$6.00\cdot10^{-7}$	90
	0.529	65.106	$5.54\cdot10^{-7}$	99
	0.578	71.598	$5.01\cdot10^{-7}$	120
	0.647	73.091	$4.58\cdot10^{-7}$	124
	0.671	73.273	$4.32\cdot10^{-7}$	124
	0.716	74.791	$4.16\cdot10^{-7}$	129
$Co(3\text{-}COONa)_4Pc$	0.304	56.034	$3.58\cdot10^{-6}$	84
	0.38	59.567	$3.31\cdot10^{-6}$	95
	0.43	60.129	$3.11\cdot10^{-6}$	96
	0.578	65.156	$2.61\cdot10^{-6}$	112
	0.647	67.056	$2.24\cdot10^{-6}$	117
	0.708	68.495	$1.88\cdot10^{-6}$	120
$Co(4\text{-}SO_3Na)_4Pc$	0.12	92.052	$8.75\cdot10^{-5}$	231
	0.391	111.947	$4.43\cdot10^{-5}$	292
	0.428	115.800	$3.83\cdot10^{-5}$	304
	0.476	116.928	$3.07\cdot10^{-5}$	306
	0.502	118.107	$2.69\cdot10^{-5}$	309
	0.578	120.833	$1.50\cdot10^{-5}$	313
	0.647	130.931	$3.87\cdot10^{-6}$	336
	0.671	149.958	$7.55\cdot10^{-8}$	367

[a] The relative error of measurement of ΔH, ΔS, and K is 2, 5, and 6%, respectively.

[b] In kJ mol^{-1}.

[c] In J mol^{-1} K^{-1}.

ies[16—18] that dimerization of the complexes Cu(4-COONa)$_4$Pc, Zn(4-COONa)$_4$Pc, Zn(4-SO$_3$Na)$_4$Pc, Zn(3-COONa)$_4$Pc, Cu(3,5-COONa)$_8$Pc, and Zn(4,5-COONa)$_8$Pc proceeds according to the π—π-type. The stability of the so-called contact or π—π-dimers is determined by the efficiency of π—π-interaction between the phthalocyanine macrocycles and the electrostatic repulsion between likely charged peripheral substituents of adjacent phthalocyanine molecules. As can be seen from the data obtained (see Table 1), an increase in the ionic strength of solution efficiently prevents dissociation of the dimeric MPc structures. Probably, the addition of an electrolyte decreases the repulsion of the peripheral substituents of the adjacent molecules to increase the stability of the dimers. Therefore, correct discussion of the effect of NaCl on the aggregation process needs an information on the mechanism of the salt effect on the ionization of the peripheral substituents in the MPc macrocycle. It is known[19] that the addition of a salt decreases the dielectric constant of the medium. It seems reasonable that precisely this factor decreases the degree of ionization of the peripheral substituents. The dielectric constant of solutions can be changed without a change in the qualitative composition of the medium by heating the solution. For example, the temperature increase by 100 °C decreases the dielectric constant, on the average, by 1.5 times.[19] Therefore, we recorded the EAS of solutions of MPc at different temperatures (25—80 °C). The observed spectral changes for all studied zinc(II) and copper(II) phthalocyanines are similar. The EAS of Zn(4,5-COONa)$_8$Pc in a borate buffer solution with an increase in the temperature is presented in Fig. 1. The observed decrease in the absorption intensity of the Q band in the EAS of ZnPc indicates a decrease in the amount of ZnPc in the monomeric form but these spectral changes are much lower than the changes caused by the addition of NaCl to a borate buffer solution of ZnPc (Fig. 2). Dotted lines in Figs 1 and 2 designate the EAS of solutions of Zn(4,5-COONa)$_8$Pc with the same dielectric constant. Two conclusions can be drawn from these data. First, the role of electrolytes in the dimerization of phthalocyanines cannot be reduced only to a change in the dielectric constant of solutions. Probably, an increase in the ionic strength of a solution increases the density of the ion atmosphere and enhances the localization of Na$^+$ ions around the negatively charged peripheral substituents of MPc; ion pairs of triples can also form. However, the current state of the theory of electrolytes[20] does not provide a description of so complicated multicomponent systems containing ions Na$^+$, MPc^{n-}, B$_4$O$_7$$^{2-}$, OH$^-$, Cl$^-$, and others. Therefore, the problem about the mechanism of the effect of electrolytes on the state of MPc in aqueous solutions and its quantitative description remains un-

Fig. 1. Electronic absorption spectrum of Zn(4,5-COONa)$_8$Pc in a borate buffer solution on heating from 25 to 80 °C; the Q band is marked by arrow.

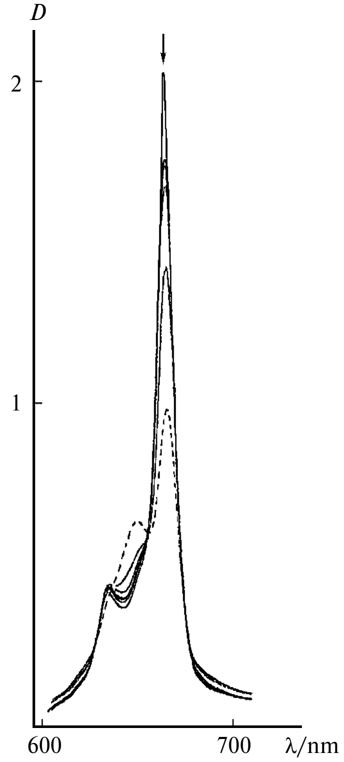


Fig. 2. Electronic absorption spectrum of Zn(4,5-COONa)$_8$Pc in a borate buffer solution upon the addition of NaCl; the Q band is marked by arrow.

solved. Second, it is evident that no correct data on the thermodynamics of MPc dimerization can be obtained for water-soluble MPc by electron spectroscopy, because a change in the temperature changes the ionization state of the peripheral substituents and electron density redistribution in the macroring; therefore, the $K = f(1/T)$ plot is nonlinear, and ΔH cannot correctly be determined by van´t Hoff´s equation.

The dissociation of the phthalocyanine dimers is endothermic (see Table 1), which assumes the donor-acceptor character of the interaction between the phthalocyanine molecules in the dimer. This conclusion agrees with the results of studying the physicochemical properties of MPc in aqueous-pyridine solutions.[21]

At the ionic strength (I) <0.5 for the systems containing Zn(4-COONa)$_4$Pc, Zn(4,5-COONa)$_8$Pc, Zn(4-SO$_3$H)$_4$Pc, and Cu(4-COONa)$_4$Pc, the function $\Delta H = f(I)$ is described by a linear equation with the correlation coefficient (R^2) at least 0.99. For Zn(3-COONa)$_4$Pc and Cu(3,5-COONa)$_8$Pc, the dependence of the change in the enthalpy of (Zn(3-COONa)$_4$Pc)$_2$ and (Cu(3,5-COONa)$_8$Pc)$_2$ dissociation on the ionic strength of a solution is monotonic but not linear ($R^2 \leq 0.8$). Evidently, the thermodynamic characteristics of the process under study for Zn(3-COONa)$_4$Pc and Cu(3,5-COONa)$_8$Pc are strongly affected by a bulky carboxyl substituent in position 3 of the macroring, along with the ionization state of the peripheral substituents. Such a substituent in position 3 violates the planar character of the macroheterocycle and prevents an efficient π—π-interaction between the aromatic MPc molecules in the dimer.

The changes in the enthalpy of the processes under study were approximated to the zero ionic strength by the ΔH values obtained from the linear regions (to ionic strengths values of 0.5 or 0.3 for the systems containing Zn(3-COONa)$_4$Pc and Cu(3,5-COONa)$_8$Pc). The resulting ΔH^0 values are presented in Table 2.

The plot of the dissociation constants of the MPc dimers *vs.* the ionic strength ($I \leq 0.5$) is linear for all studied MPc. The K^0 values obtained by the approximations of the revealed dependences to $I = 0$ are presented in Table 2. The $K = f(I)$ plots are described by the equations

$$K = -1.5599 \cdot 10^{-6} I + 1.3119 \cdot 10^{-6}\ (R^2 = 0.999), \qquad (2)$$
$$K = -3.5772 \cdot 10^{-8} I + 3.9358 \cdot 10^{-8}\ (R^2 = 0.998), \qquad (3)$$
$$K = -1.530 \cdot 10^{-6} I + 1.9194 \cdot 10^{-6}\ (R^2 = 0.998), \qquad (4)$$
$$K = -328.4 I + 239.3\ (R^2 = 0.966), \qquad (5)$$
$$K = -1.5816 \cdot 10^{-8} I + 1.0596 \cdot 10^{-8}\ (R^2 = 0.998), \qquad (6)$$
$$K = -9.1943 \cdot 10^{-5} I + 1.4704 \cdot 10^{-4}\ (R^2 = 0.995) \qquad (7)$$

for Zn(4-SO$_3$Na)$_4$Pc, Zn(4-COONa)$_4$Pc, Zn(3-COONa)$_4$Pc, Zn(4,5-COONa)$_8$Pc, Cu(4-COONa)$_4$Pc, and Cu(3,5-COONa)$_8$Pc, respectively.

The coefficients at I in Eqs (2)—(7) do not allow us to assess the sensitivity of the phthalocyanine-containing systems to anion-cationic interactions. This is due to the fact that the K^0 values obtained for the MPc under study are of different order and, hence, the contribution of the first term in Eqs (2)—(7) to K is different. The $K^0/K(I)$ values presented in Table 2 can serve as true characteristics of the MPc sensitivity to anion-cationic interactions. The sensitivity of the MPc to anion-cationic interactions increases in the following series: Cu(3,5-COONa)$_8$Pc < < Zn(3-COONa)$_4$Pc < Zn(4-COONa)$_4$Pc < Zn(4-SO$_3$Na)$_4$Pc < Zn(4,5-COONa)$_8$Pc < Cu(4-COONa)$_4$Pc. When the peripheral substituents of MPc (Cu(3,5-COONa)$_8$Pc, Zn(3-COONa)$_4$Pc) induce the macrocycle deformation and thus create steric hindrance for the π—π interaction between the phthalocyanine molecules, the effect of the anion-cationic interactions of the COO$^-$ substituents with the ion environment becomes less significant. When the planarity of the macrocycle is not violated (Zn(4-COONa)$_4$Pc and Zn(4,5-COONa)$_8$Pc), the octasubstituted MPc are more sensitive to the ion environment compared to the tetrasubstituted MPc and,

Table 2. Standard thermodynamic characteristics of the dissociation of the MPc dimers in a borate buffer solution

MPc	K^0	ΔH^0 /kJ mol^{-1}	ΔS^0 /J mol^{-1} K^{-1}	K^0/K_I ($I = 0.5$)
Zn(4-COONa)$_4$Pc	$3.94 \cdot 10^{-8} \pm 4 \cdot 10^{-10}$	77.83±3.86	119±10	1.9
Zn(4-SO$_3$Na)$_4$Pc	$1.31 \cdot 10^{-6} \pm 3 \cdot 10^{-8}$	98.36±5.63	217±12	2.5
Zn(3-COONa)$_4$Pc	$1.92 \cdot 10^{-6} \pm 7 \cdot 10^{-8}$	68.92±2.98	122±20	1.6
Zn(4,5-COONa)$_8$Pc	239±70	18.60±6.44	108±20	3.2
Cu(4-COONa)$_4$Pc	$1.06 \cdot 10^{-8} \pm 2 \cdot 10^{-10}$	122.00±19.23	257±15	3.9
Cu(3,5-COONa)$_8$Pc	$1.47 \cdot 10^{-4} \pm 1 \cdot 10^{-6}$	90.36±7.72	230±22	1.5
OHAl(4-COONa)$_4$Pc	$1.47 \cdot 10^{-5} \pm 3 \cdot 10^{-7}$	59.79±1.85	108±18	1.3
Co(4-COONa)$_4$Pc	$9.01 \cdot 10^{-7} \pm 1 \cdot 10^{-8}$	49.73±2.95	51±20	1.5
Co(3-COONa)$_4$Pc	$4.65 \cdot 10^{-6} \pm 2 \cdot 10^{-8}$	47.31±2.76	57±14	1.6
Co(4-SO$_3$Na)$_4$Pc	$1.06 \cdot 10^{-4} \pm 5 \cdot 10^{-6}$	84.05±4.53	206±31	3.9

probably, interact more efficiently (than the tetrasubstituted analogs) with the protein molecules due to the electrostatic forces. Another approach has previously been proposed[22,23] to estimate the ionic strength effect on the state of macroheterocyclic molecules (porphyrins, phthalocyanines) in solutions. It was assumed[22—24] that the dependence of the dimerization constant (K_{dim}) on the ionic strength for the water-soluble macroheterocycles is rather well described, in the first approximation, by the limiting Debye—Hückel equation

$$\log K_{\mathrm{dim}} = (\lg K^0_{\mathrm{dim}} + 2AZ_AZ_BI^{0.5})/(1 + I^{0.5}), \quad (8)$$

where Z_A and Z_B are the charges of the phthalocyanine molecules in the dimer composition.

Using formula (8), the authors calculated[22—27] the effective charge of porphyrin molecules in a dimer composition. For instance, for tetracation porphyrins at a formal charge of 4+, the real charge ranges from 2+ to 3+, depending on the nature of the porphyrin macrocycle and ionic strength of the medium.[22—27] Unfortunately, the authors of these works did not discuss the revealed regularities from the viewpoint of the effects of the nature of interacting molecules and only restricted their consideration by stating the fact: the Debye—Hückel equation is valid in the case of porphyrins, whose salt-induced dimerization begins at small amounts of salt additives. It should be noted that the application of the Debye—Hückel theory to water-soluble macroheterocycles needs an additional substantiation. This theory was developed for 1,1-electrolytes in a concentration limit below 0.024 mol L^{-1} according to estimates[28] and, according to other estimates,[29] below 10^{-4} mol L^{-1}. In the cited works,[22—27] the dimerization of metal porphyrins in aqueous media was studied in solutions containing 2 and 5 mol L^{-1} of NaCl only. In addition, K_{dim} of the metal porphyrins were determined by electron absorption spectroscopy with several assumptions: (*i*) the molar absorption coefficient of the monomer (ε_m) was found in ultimately dilute solutions ignoring dimeric structures; (*ii*) for strongly aggregating substances ($K_{\mathrm{dim}} > 10^4$) ε_m values obtained in solutions of detergents were used; (*iii*) the molar absorption coefficient of the dimer (ε_d) was determined by the addition of a large amount of the salt or an increase in the macroheterocycle concentration in a solution; (*iv*) the presence of higher aggregates was ignored; (*v*) dependences of ε_m and ε_d of MPc on the ionic strength were ignored, *etc*. All these assumptions depreciate the results of studies[22—27] and explain substantial differences in data published for the same systems.

A comparative analysis of the K^0 values (see Table 2) obtained for zinc(II) phthalocyanines makes it possible to estimate the effect of the number and position of the peripheral functional substituents on the aggregation ability of MPc. The tendency of $(MPc)_2$ to dissociate in solutions decreases in the series

$$\mathrm{Zn(4,5\text{-}COONa)_8Pc > Zn(3\text{-}COONa)_4Pc >}$$
$$\mathrm{> Zn(4\text{-}SO_3Na)_4Pc > Zn(4\text{-}COONa)_4Pc.} \quad (9)$$

The zinc(II) phthalocyanine molecule contains eight charged functional groups, which is sufficient to provide an efficient electrostatic repulsion between the adjacent charged substituents of the adjacent molecules, due to which the $Zn(4,5\text{-}COONa)_8Pc$ complex exists predominantly in the monomeric form in the solutions under study. On the contrary, tetrasubstituted sulfo- and carboxyphthalocyanines are mainly dimeric even at the zero ionic strength. The higher affinity revealed in this work for carboxyphthalocyanines ($Zn(4\text{-}COONa)_4Pc$) to aggregate in aqueous media compared to their sulfosubstituted analogs ($Zn(4\text{-}SO_3Na)_4Pc$) was repeatedly mentioned[30,31] when the EAS of MPc were analyzed. Probably, the sulfo groups, whose van der Waals radius exceeds by ~1.4 times that of the carboxyl substituents,[32] prevent the π—π-interaction between two aromatic systems of phthalocyanine molecules in the dimeric structure; therefore, the $(Zn(4\text{-}SO_3Na)_4Pc)_2$ dimer is thermodynamically less stable than the dimer $(Zn(4\text{-}COONa)_4Pc)_2$. The negative effect of the steric factor created by the carboxyl group in position 3 of the macrocycle on the thermodynamic stability of the phthalocyanine dimer was discussed above.

The bond cleavage energy for the dimeric phthalocyanines decrease in the following series:

$$\mathrm{Zn(4\text{-}SO_3Na)_4Pc > Zn(4\text{-}COONa)_4Pc >}$$
$$\mathrm{> Zn(3\text{-}COONa)_4Pc > Zn(4,5\text{-}COONa)_8Pc.} \quad (10)$$

This series, except for the position of the sulfosubstituted phthalocyanine derivative, coincides with series (9). The changes in K and ΔH during $(Zn(4\text{-}SO_3Na)Pc)_2$ and $(Zn(4\text{-}COONa)_4Pc)_2$ dissociation are not parallel, probably, due to specific interactions of the peripheral substituents of the phthalocyanines with water molecules. Since the sulfo group is less prone to form hydrogen bonds with proton-donor substituents than the carboxyl group,[17,33] the dissociation of dimers of the carboxysubstituted phthalocyanines is lower energy consuming than the sulfosubstituted phthalocyanines.

A special group among the MPc studied is composed by cobalt(II) and aluminum(III) phthalocyanines. Unlike the complexes of Zn^{2+} and Cu^{2+} with phthalocyanines, these macrocycles can form dimers of different types. In the case of $HOAl(4\text{-}COONa)_4Pc$, the π—π-type dimers $(HOAl(4\text{-}COONa)_4Pc)_2$ and μ-oxo dimers $(Al(4\text{-}COONa)_4Pc)_2O$ were reliably characterized by X-ray diffraction[34,35] and spectral data.[36,37] The electronic spectra of different $Al^{III}Pc$ dimers contain characteristic bands, and the Q band of the π—π-dimer

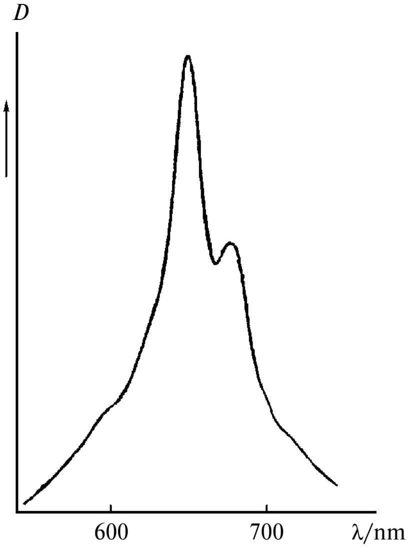


Fig. 3. Electronic absorption spectrum of HOAl(4-COONa)$_4$Pc in a borate buffer solution.

HOAl(4-COONa)$_4$Pc has an absorption maximum at λ_{max} = 638 nm, while for the μ-oxo dimer λ_{max} = 648 nm. Our spectral study indicates that HOAl(4-COONa)$_4$Pc in borate buffer solutions form μ-oxo dimers (Fig. 3). The EAS of HOAl(4-COONa)$_4$Pc exhibit relaxation effects, and the aggregation was equilibrated within 4 h. The obtained results agree with the kinetic data for the μ-oxo-dimerization of HOAl(4-COONa)$_4$Pc. It is of interest that, unlike the π—π-dimers (ZnPc)$_2$ and (CuPc)$_2$, the heating of solutions containing HOAl(4-COONa)$_4$Pc increases the absorption intensity of both the dimer (λ_{max} = 648 nm) and monomer (λ_{max} = 686 nm). On heating the solution for 7—10 h at the temperature >80 °C, the EAS of HOAl(4-COONa)$_4$Pc exhibited a decrease in the absorption intensity at λ = 648 nm, indicating a decrease in the content of the phthalocyanine dimeric form.

Phthalocyanine complexes containing metal ions with unfilled external electronic shells, such as Co^{2+}, is more complicated case. This is caused in part by restricted experimental techniques suitable for determining the aggregation properties and types of the CoPc dimers. For instance, a comparative analysis of the emission and electronic absorption spectra of HOAl(4-COONa)$_4$Pc unambiguously reveals the presence of aggregation equilibria and also the type of dimerization.[36] Unlike this, CoPc does not fluoresce in either the monomeric or dimeric form and, hence, the mode of CoPc dimerization cannot be concluded from the emission spectra. Excess alkali necessary for the dissolution of carboxysubstituted cobalt(II) phthalocyanines does not allow one to record the NMR and Raman spectra of CoPc samples. The type of CoPc dimerization cannot be interpreted unambiguously from the ESR spectra of frozen solutions of CoPc. For example, for CoPc the authors[6,38,39] determined the factor of spectroscopic splitting sensitive to the ligand environment of the Co^{2+} ion (g = 2.0034—2.0040). However, this singlet line can be originated from both defects in the crystalline lattice of the sample and formation of a molecular complex CoPc•O$_2$ or a μ-oxo dimer PcCo—O—CoPc.[6,38,39]

The carboxy- and sulfosubstituted cobalt(II) phthalocyanines under study demonstrate different spectral behavior. In the case of Co(4-COONa)$_4$Pc and Co(3-COONa)$_4$Pc, the relaxation effects were observed for 4—5 h. By contrast, the EAS of the Co(4-SO$_3$Na)$_4$Pc complex in a borate buffer solution changed for a much longer time (~10—12 h). Various spectral changes are induced by heating borate buffer solutions of the carboxy- and sulfosubstituted cobalt(II) phthalocyanines. The spectral changes observed in buffer solutions of Co(4-COONa)$_4$Pc and Co(3-COONa)$_4$Pc with the temperature increase are similar to the changes in the spectra of HOAl(4-COONa)$_4$Pc, *i.e.*, the heating of phthalocyanine-containing solutions to 50 °C is accompanied by an increase in the absorption intensity of both the monomeric and dimeric forms of MPc; the further temperature increase results in a sharp increase in the absorption intensity of the dimer.

The electronic absorption spectrum of cobalt(II) tetra-4-sulfophthalocyanine in a borate buffer solution contains two bands with absorption maxima at 613 nm (Q$_d$ is the band of the dimer) and 667 nm (Q$_m$ is the band of the monomer). The ratio of intensities of the absorption bands Q$_d$ and Q$_m$ ($\varepsilon_d : \varepsilon_m$) is 5.4, *i.e.*, in a borate buffer solution cobalt(II) tetra-4-sulfophthalocyanine exists predominantly in the dimerized state. An increase in the temperature of a solution of Co(4-SO$_3$Na)$_4$Pc induces spectral changes similar to those described above for zinc(II) and copper(II) phthalocyanines and corresponding to an increase in the content of the cobalt(II) tetra-4-sulfophthalocyanine dimers. The electronic absorption spectrum of Co(4-SO$_3$Na)$_4$Pc is transformed on heating into a single-band spectrum with λ_{max} = 613 nm.

The electronic absorption spectra of aqueous solutions of cobalt(II) tetra-4-carboxyphthalocyanines have repeatedly been documented. The EAS of Co(4-SO$_3$H)$_4$Pc in solvents of different nature and their mixtures with water were studied,[40,41] and the following assignment of bands was proposed: the spectrum of Co(4-SO$_3$H)$_4$Pc in the monomeric form has an absorption maximum at λ_{max} = 663 nm, Co(4-SO$_3$H)$_4$Pc•O$_2$ exhibits λ_{max} = 670 nm, and the spectra of the Co(4-SO$_3$H)$_4$Pc dimers D and D´ are characterized by λ_{max} = 626 and 610—616 nm, respectively. It was assumed[40] that the differences in the EAS of D and D´ of Co(4-SO$_3$H)$_4$Pc are caused by different orientations of two phthalocyanine molecules in the corresponding dimers. The type of dimerization including 12 water molecules was proposed for dimer D

$$2\,\mathrm{Co(4\text{-}SO_3H)_4Pc} + 12\,\mathrm{H_2O} \xrightleftharpoons{K_{\mathrm{dim}}} \mathrm{(Co(4\text{-}SO_3H)_4Pc)_2\cdot(H_2O)_{12}}.$$

The process was studied in mixed water—alcohol (methanol, ethanol) solvents. The presence of alcohol in this equilibrium was ignored, although it is known that these are precisely the alcohol molecules which can be involved in the dimerization processes of macroheterocyclic compounds forming hydrogen bonds with the peripheral oxygen-containing substituents.[17,18] In addition, a possibility of hydration of MPc molecules in the monomeric form was not considered.[40] The following arguments confirm that water is specifically bound in a dimer molecule: $\log(K_{\mathrm{dim}})$ does not linearly correlate with the water activity (partial H_2O vapor pressure in a mixed water—alcohol solvent is taken as the activity of water); $\log(K_{\mathrm{dim}})$ does not correlate linearly with the electrostatic repulsion value (electrostatic repulsion was determined as $1/\varepsilon$, where ε is the dielectric permeability of the medium). Evidently, these arguments, as well as the assumptions made by the authors, can be criticized. The arrangement of cobalt(II) tetra-4-sulfophthalocyanine molecules in the D′ dimer and the character of intermolecular interaction of the phthalocyanines were not discussed in the works.[40,41] Our spectral characteristics (λ_{max} = 613 nm) coincide with similar data[40] for the D′ dimer. As shown previously,[40] the D′ dimer of $\mathrm{Co(4\text{-}SO_3H)_4Pc}$ can be obtained in protic (ethanol, propanol) and aprotic solvents ($\mathrm{Me_2CO}$, DMSO) under the necessary condition of a restricted solubility of $\mathrm{Co(4\text{-}SO_3H)_4Pc}$ in these solvents. According to the results obtained in the present work, the D′ dimer of $\mathrm{Co(4\text{-}SO_3H)_4Pc}$ is formed in borate buffer solutions. Analysis of our and literature data assumes that the D′ dimer of $\mathrm{Co(4\text{-}SO_3H)_4Pc}$ is a π—π-dimer.

The thermodynamic characteristics of dissociation of the dimers of $\mathrm{Co^{II}}$ and $\mathrm{HOAl^{III}}$ phthalocyanines are presented in Table 1. An increase in the NaCl concentration in phthalocyanine-containing solutions, regardless of the dimerization type, increases the thermodynamic stability of the dimers, which is satisfactorily described by linear equations

$$K = -3.1173\cdot10^{-5}I + 7.4123\cdot10^{-5}\ (R^2 = 0.985), \quad (11)$$
$$K = -6.4028\cdot10^{-7}I + 9.0749\cdot10^{-7}\ (R^2 = 0.997), \quad (12)$$
$$K = -3.5576\cdot10^{-6}I + 4.6551\cdot10^{-6}\ (R^2 = 0.999), \quad (13)$$
$$K = -1.5846\cdot10^{-4}I + 1.0635\cdot10^{-4}\ (R^2 = 0.999) \quad (14)$$

for $\mathrm{HOAl(4\text{-}COONa)_4Pc}$, $\mathrm{Co(4\text{-}COONa)_4Pc}$, $\mathrm{Co(3\text{-}COONa)_4Pc}$, and $\mathrm{Co(4\text{-}SO_3Na)_4Pc}$, respectively.

However, the dimeric structures of the $\mathrm{Co^{II}}$ and $\mathrm{HOAl^{III}}$ phthalocyanines have different sensitivities to an increase in the ionic strength (see Table 2). An increase in the ionic strength to 0.5 enhances the thermodynamic stability of the μ-oxo dimers of MPc by 1.5 times, on the average, while the stability of the π—π-dimer of $\mathrm{Co(4\text{-}SO_3Na)_4Pc}$ increases by ~4 times. It is most likely that the degree of neutralization of the peripheral substituents of MPc, dimerizing according to the μ-oxo type, is not a determining factor.

It is clearly seen for $\mathrm{Co(4\text{-}SO_3Na)_4Pc}$ and $\mathrm{Co(4\text{-}COONa)_4Pc}$ considered as examples that differences in the nature of the peripheral substituents can exert such a strong effect on MPc as a whole that MPc containing different functional substituents form aggregates (dimers) of different type under identical conditions. As shown by numerous kinetic data for the formation of μ-oxo dimers of MPc and metal porphyrins,[36,42,43] the higher the residual positive charge on the metal ion, the higher the affinity to O_2 and the more easily the μ-oxodimerization occurs. Based on the Hammett constants, one can conclude that the polar effect of the sulfo group is higher than that of the carboxyl group.[44] Therefore, four sulfo groups in a phthalocyanine molecule should decrease the electron density on the nitrogen atoms of the reaction center more efficiently, weakening the σ-Co←N bond, increasing the residual positive charge on the $\mathrm{Co^{2+}}$ ion, and enhancing its coordination ability. However, we obtained contradictory results: namely, the coordination ability of $\mathrm{Co(4\text{-}COONa)_4Pc}$ toward electron-donor ligands is higher than that of $\mathrm{Co(4\text{-}SO_3Na)_4Pc}$. The phthalocyanine molecule is a multicontour conjugated system in which π-electrons of the benzene rings interact very weakly with 18 central π-electrons of the macroring.[45] Therefore, the substituent effect is mainly determined by its inductive effect (−*I*) and field effect (−*F*) and is virtually independent of the conjugation effect (–*C*). For the carboxyl group, the ratio of the conjugation to inductive effect is[33] 0.25 : 0.75. On the contrary, the main contribution to the effect of the sulfo group is made[33] by the electronic effect –*C*. Therefore, in metal phthalocyanines the carboxyl groups are stronger electron-acceptor substituents than the sulfo groups.

The thermodynamic stability of the μ-oxo dimers increases in the following series: $\mathrm{HOAl(4\text{-}COONa)_4Pc} <$ $< \mathrm{Co(3\text{-}COONa)_4Pc} < \mathrm{Co(4\text{-}COONa)_4Pc}$. The stability constant of $\mathrm{(Co(4\text{-}COONa)_4Pc)_2O}$, which by more than order of magnitude exceeds a similar characteristic for $\mathrm{(Co(3\text{-}COONa)_4Pc)_2O}$, indicates the efficient transfer of the negative inductive effect of the carboxyl substituent in position 4 of the macrocycle, decreasing, as mentioned above, the electron density on the nitrogen atoms of the reaction center of phthalocyanine, increasing the residual positive charge on the $\mathrm{Co^{2+}}$ ion, and enhancing the coordination ability of the $\mathrm{Co^{2+}}$ ion toward oxygen. It is of interest that the enthalpy components (ΔH^0) of the dissociation of $(Co(3\text{-}COONa)_4Pc)_2O$ and $(Co(4\text{-}COONa)_4Pc)_2O$ coincide within an error. The dissociation of the $(Al(4\text{-}COONa)_4Pc)_2O$ dimer is accompanied by higher (compared to those of $(CoPc)_2O$) energy expenses, which is probably caused by the necessity to have a counterion or covalently linked ligand in the case of a tricharged metal ion.

Thus, in this work, the standard thermodynamic characteristics of aggregation processes for the series of water-soluble macroheterocycles were obtained for the first time by the direct experimental method. It is established that the introduction in position 3 of the macrocycle of the peripheral substituents violating planarity of the phthalocyanine macrocycle or an increase in the number of charged functional substituents of MPc favors the shift of the aggregation equilibria toward the formation of MPc monomers. It is shown that one of the most important factors in the stabilization of the π—π-dimers of MPc are anion-cationic interactions of MPc. The quantitative dependences revealed for the stability constants of the metal phthalocyanine dimers *vs.* ionic strength of the medium are basic for controlling the aggregation state of MPc in solutions.

The results and conclusions obtained in this work can help in the use of water-soluble MPc as photosensors and catalysts and for studying the biochemical activity of MPc. The quantitative dependence of the aggregation properties of MPc on the ionic strength of the medium makes it possible to decrease the number of works searching for MPc as potential medicinal preparations for the inactivation of bacteria and viruses.

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