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Determination of the dimerization constants of water soluble metallophthalocyanines by calorimetric titration using electron-donating ligands

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The thermodynamics of dimerization of zinc(II) tetra-4-carboxyphthalocyanine in aqueous solutions and its solvation interactions with electron-donating pyridine molecules were studied by calorimetry.

Water soluble phthalocyanines and their metallocomplexes (MPc) are photosensors and catalysts. However, their photochemical and catalytic activity decreases many times due to aggregation.[1,2] The dispersity of metallophthalocyanine systems can be increased by (i) the steric separation of macromolecules by intercalation and encapsulation[3,4] and (ii) the addition of detergents and electron-donating ligands to phthalocyanine-containing solutions.[1,5] The intermolecular interactions of MPc with electron-donating molecules are difficult to study because most of physico-chemical methods are insensitive to low energetic solvation interactions of MPc with molecular ligands. For instance, it is impossible to measure the NMR spectra of carboxy-substituted metallophthalocyanines in aqueous solutions due to presence of an alkali, which is required for dissolving them in water. Electronic absorption spectra cannot be used due to the photodestruction of MPc.[1,6,7] Moreover, temperature changes cause a decrease in the dielectric permittivity of solutions.[8] This changes the state of aggregation of charged phthalocyanine molecules. Herefore, we studied the aggregation of the sodium salt of zinc(II) tetra-4-carboxyphthalocyanine [$Zn(4\text{-}COONa)_4Pc$] in aqueous alkaline and borate buffer solutions

$$(\mathrm{MPc})_2 \xleftrightarrow{K_1} \mathrm{MPc} + \mathrm{MPc} \qquad (1)$$

and the influence of the molecular complexation of $Zn(4\text{-}COONa)_4Pc$ with pyridine in aqueous solution: (2)

$$\mathrm{MPc} + \mathrm{L} \xleftrightarrow{K_2} \mathrm{MPc \cdot L} \qquad (2)$$

on equilibrium (1) using calorimetric titration.

Calorimetric titration was performed using a highly sensitive automatic titration calorimeter.[9] The titrant was a solution of pyridine (5.3–6.1 mol dm^{-3}) in an aqueous alkali (pH 11.37) or a borate buffer solution (pH 9.65). A solution of $Zn(4\text{-}COONa)_4Pc$ (10^{-7}–10^{-6} mol dm^{-3}) in the specified media was placed in a calorimetric cell. Table 1 summarises the results. We supposed that $Zn(4\text{-}COONa)_4Pc$ molecules exist mainly as monomer and dimer species in the test solutions. The heat effects of dilution were measured separately. The phthalocyanine solution was titrated with a solvent. Endo effects due to the shift of equilibrium (1) towards monomer species were about 10^{-6} J and taken into account in calculations. The equilibrium constants are:

$$K_1 = \frac{[\mathrm{MPc}]_n^2}{[(\mathrm{MPc})_2]_n} = \frac{[\mathrm{MPc}]_n^2}{(C^0_{(\mathrm{MPc})_2})_n - 1/2[\mathrm{MPc}]_n - 1/2[\mathrm{MPc \cdot L}]_n}$$

$$K_2 = \frac{[\mathrm{MPc \cdot L}]_n}{[\mathrm{MPc}]_n[\mathrm{L}]_n} = \frac{[\mathrm{MPc \cdot L}]_n}{[\mathrm{MPc}]_n\{(C^0_\mathrm{L})_n - [\mathrm{MPc \cdot L}]_n\}}.$$

After transformations, we obtain:

$$[\mathrm{MPc}]_n^3 + [\mathrm{MPc}]_n^2\left(\frac{1}{K_2} + \frac{K_1}{2}\right) + [\mathrm{MPc}]_n\left[\frac{K_1}{2K_2} + \frac{K_1}{2}\,(C^0_\mathrm{L})_n - K_1(C^0_{(\mathrm{MPc})_2})_n\right] = \frac{K_1}{K_2}(C^0_{(\mathrm{MPc})_2})_n,$$

where $[\mathrm{MPc}]_n$, $[(\mathrm{MPc})_2]_n$, $[\mathrm{MPc \cdot L}]_n$ and $[\mathrm{L}]_n$ are the equilibrium concentrations of the metallophthalocyanine, its dimer species, molecular complex and pyridine, respectively; $(C^0_{(\mathrm{MPc})_2})_n$ and $(C^0_\mathrm{L})_n$ are the initial concentrations of the metallophthalocyanine and pyridine after *n*th injections, respectively; *n* is the injection number.

Table 1 Experimental results of titration of $Zn(4\text{-}COONa)_4Pc$ by pyridine solution in water at 298.15 K.

	Borate buffer	Water–alkaline solution
V_solut/ml	32.61761	31.72441
V_injec/ml	0.08918	0.08918
M_Py/mol dm^{-3}	5.30112	6.13361
M_ZnPc/mol dm^{-3}	0.00004312	0.00009054
Injection number	Q, J	
1	–0.0238777	0.0066468
2	–0.0148771	0.0058951
3	–0.0091724	0.0042409
4	–0.0057010	0.0029723
5	–0.0036132	0.0021339
6	–0.0023467	0.0015841
7	–0.0015629	0.0012138
8	–0.0010656	0.0009558
9	–0.0007416	0.0007703
10	–0.0005254	0.0006331
11	–0.0003776	0.0005289
12	–0.0002745	0.0004483
13	–0.0002012	0.0003846
14	–0.0001482	0.0003334
15	–0.0001094	0.0002917
16	–0.0000805	0.0002576
17	–0.0000589	0.0002287
18	–0.0000425	0.0002045
19	–0.0000299	0.0001839
20	–0.0000203	0.0001664
21	–0.0000128	0.0001512
22	–0.0000070	0.0001379
23	–0.0000025	0.0001264
24	0.0000010	0.0001162
25	0.0000038	0.0001072

The heat absorbed or evolved after the *n*th injection can be calculated as:

$$Q_n = -(\Delta H_1 V_n[\mathrm{MPc}]_n + \Delta H_2 V_n[\mathrm{MPc \cdot L}]_n), \qquad (3)$$

with the total volume V_n of the solution. An injection schedule (the number of injections, the injected volume and the time between injections) is set up with the software.

The values of K_1, K_2, ΔH_1 and ΔH_2 were computed using the least-squares method (Maple 8 program).

For the test systems, the only local minimum was determined. This fact confirms the reliability of the thermodynamic characteristics obtained (Table 2).

No concentration dependence of the thermodynamic characteristics of $Zn(4\text{-}COONa)_4Pc$ was observed in the range 10^{-7}–10^{-6} mol dm^{-3}. Changes in the aggregation of $Zn(4\text{-}COONa)_4Pc$ were studied using electronic absorption spectra (Figure 1). The dimer species of $Zn(4\text{-}COONa)_4Pc$ exhibit a *Q* band at 634 nm in comparison with monomer species (680 nm). Because of the

Table 2 Thermodynamic characteristics of the dissociation of the dimer species of Zn(4-COONa)$_4$Pc and the coordination of pyridine to Zn(4-COONa)$_4$Pc in aqueous media at 298.15 K.

Medium	$(\mathrm{MPc})_2 \xleftrightarrow{K_1} \mathrm{MPc} + \mathrm{MPc}$			$\mathrm{MPc} + \mathrm{L} \xleftrightarrow{K_2} \mathrm{MPc} \cdot \mathrm{L}$		
	K_1	ΔH_1/kJ mol^{-1}	ΔS_1/J mol^{-1} K^{-1}	K_2	ΔH_2/kJ mol^{-1}	ΔS_2/J mol^{-1} K^{-1}
Borate buffer	$1.47\times10^{-6}\pm3\times10^{-8}$	102.97±0.05	234±20	312±7	–72.35±0.03	–195±7
Water–alkaline solution	$6.10\times10^{-6}\pm2\times10^{-8}$	76.79±0.04	158±15	376±10	–73.22±0.02	–196±9

overlapping of the *Q* bands of monomer and dimer species, it is impossible to estimate the amounts of monomers and dimers from molar absorption coefficients.

As can be seen in Table 1, the thermodynamic characteristics of process (1) and (2) depend on the solution composition. The replacement of a borate buffer (pH 9.65) with a water-alkaline solution (pH 11.37) leads to an increase in the dissociation constant of the aggregated phthalocyanine molecules. Obviously, a strong influence of pH on the aggregation and solubility of the metallophthalocyanines is caused by the high proton affinity of peripheral carboxyl substituents in Zn(4-COONa)$_4$Pc (p*K*a is 4.6–4.8[11]).

This conclusion agrees with spectral characteristics[12] for water-alkaline solutions of Zn(4-COONa)$_4$Pc.

Specific donor–acceptor interactions of Zn(4-COONa)$_4$Pc with pyridine in borate buffer result in the formation of thermodynamically stable complexes in comparison with those in water–alkaline medium. The ionic strength of the borate buffer (I) is equal to 0.12, while that of the water-alkaline solution is 0.0023. Probably, the increase of the ionic strength of the solvent promotes the neutralization of the peripheral carboxylic substitutes of Zn(4-COONa)$_4$Pc. Salt-induced neutralization of functional porphyrine molecules is well known. Thus, the formal charge of a porphyrine molecule is –4, while the real charge varies from –3 to –2 depending on the macrocyclic ring and the ionic strength of solution.[13–15] An analogous phenomenon may be characteristic of phthalocyanine molecules. Thus, as the ionic strength increases, the negative charges of carboxylic substituents become neutralized and their electron-accepting ability in relation to the phthalocyanine macrocycle decreases. This leads to an increase in the strength of $\mathrm{Zn}^{2+}\leftarrow\mathrm{Pc}$ bonds and a decrease in the residual positive charge at the Zn^{2+} ion. Consequently, the coordination ability of a central metal atom in relation to electron-donating pyridine molecules reduces. High enthalpy changes and relatively low thermodynamic stability of the molecular complexes of Zn(4-COONa)$_4$Pc with pyridine should be noted. This fact can be explained by competition between the dimerization of phthalocyanine molecules and their complexation with pyridine. The values of ΔS_1 and ΔS_2 are typical of dissociation and association processes, respectively.

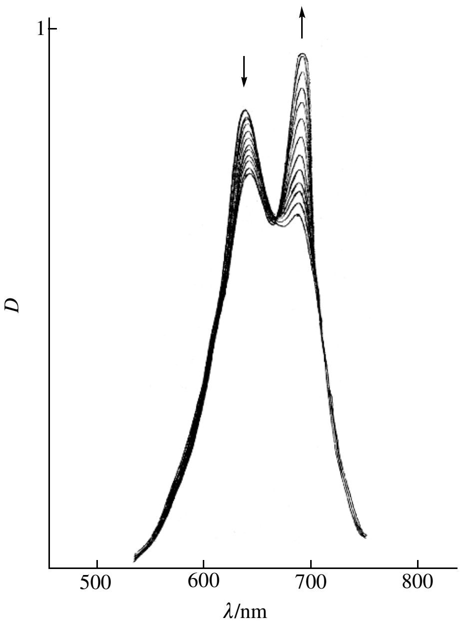

Figure 1 Electronic absorption spectrum of Zn(4-COONa)$_4$Pc in an aqueous borate buffer on the addition of pyridine.

Thus, Zn(4-COONa)$_4$Pc forms a thermodynamically stable complex with pyridine. Specific interactions of Zn(4-COONa)$_4$Pc with pyridine shift the aggregation equilibrium towards monomer metallophthalocyanine species. The ability of Zn(4-COONa)$_4$Pc to coordinate electron-donating molecules in aqueous solutions decreases with increasing ionic strength of the medium.

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