Effect of electric permittivity of the solvent on aggregation process of the water-soluble sulfonated metal phthalocyanines

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ABSTRACT

Dimerization of sulfonated phthalocyanines of divalent metals (Zn, Cu, and Co) in binary water-alcohol solutions was studied by spectroscopic techniques. The dimerization manifests itself in changes in the absorption spectra and in a decrease of fluorescence intensity. The equilibrium constants of dimerization depend on the electric permittivity of the solvent and on degree of sulfonation. The process can be semi-qualitatively described by a simple model taking into account solvation and electrostatic interactions between phthalocyanine anions. The effect of electric permittivity has not been observed in sulfonated Al and Si phthalocyanines. Experimentally determined fluorescence quantum yields in alcoholic solutions range between 0.74 and 0.015.

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1. Introduction

Phthalocyanines (Pcs, see Fig. 1a) are a family of materials attracting much attention in recent years (see, e.g., [1–4] for collections of reviews). The interest has been associated, to a great extent, with emerging applications of these materials in various modern technologies ranging from catalysis to electronics to medicine.

Applicability of unsubstituted Pcs is limited by lack of solubility in common solvents. This obstacle, however, may be overcome by functionalization with suitable side groups. In particular, substitution with hydrophilic (e.g., sulfonate) groups makes them soluble in water, thus paving the way to biological applications. Many soluble phthalocyanines tend to aggregate in solutions. The aggregation, apart from being an interesting phenomenon per se, is also important from the point of view of possible applications of these materials in medicine.

One of important emerging fields of application of soluble Pcs is the photodynamic therapy (PDT). PDT offers an alternative for the treatment of cancer, employing a combination of light and a drug ('photosensitizer') to selectively destroy tumor tissue. Upon illumination, the photosensitizer is excited to a higher electronic state, the excitation resulting eventually in the formation of radicals (type I reactions) or of singlet oxygen (type II reactions). An extensive review on photosensitized singlet oxygen has been published in [5].

Some properties of Pcs making them useful as prospective PDT materials are determined by the nature of the central ion (e.g., the quantum yield of formation of the triplet state and its lifetime). It should be realized, however, that the photophysical properties of solutions of Pcs are also modified by the degree of their aggregation (thus, indirectly, by the nature and number of the side groups). The latter factor critically affects applicability of these materials in PDT because excitation of an aggregate is preferentially followed by efficient internal conversion to the ground state [6]. Thus understanding (and, possibly, control of) factors influencing the aggregation of Pcs in solution is of importance for the choice of suitable materials and conditions of their use in PDT.

The effect of solvents on the state of aggregation of soluble Pcs was recognized quite early, and since then has been studied by several groups and reported in numerous papers (e.g., [7–20], see also [6,21,22] for reviews). Most of recent research has been carried out in non-aqueous solvents as it was recognized that the dimerization (and then formation of higher aggregates) of many phthalocyanines takes place more readily in aqueous solutions [7–9] (see also the review [21]). Recent reports on syntheses of water-soluble Pcs can nevertheless be found in the literature [23], the aggregation being prevented by insertion of bulky substituents.

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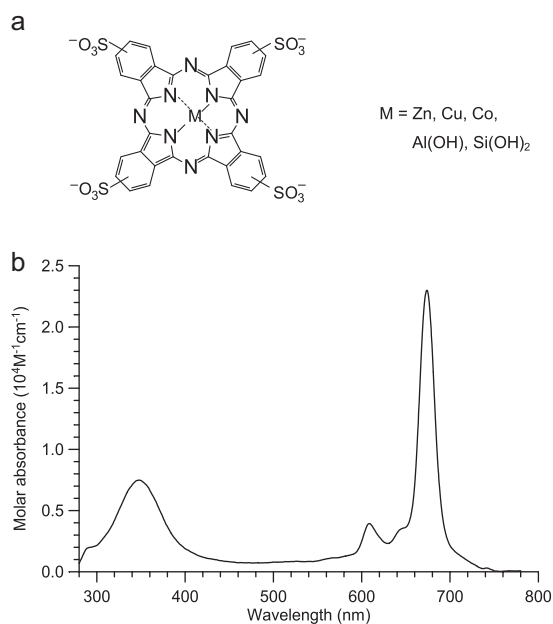
Fig. 1. (a) Formula of tetrasulfonated phthalocyanine anion. (b) Exemplary absorption spectrum of diluted solution of ZnPcS$_4$ in ethanol ($c \approx 6.5 \times 10^{-6}$ M), covering the spectral regions of the Soret band and of the Q band.

One may envisage that the aggregation may be affected either by specific interactions of solvent molecules with Pc molecules (e.g., by formation of hydrogen bonds to central ions or to peripheral nitrogen atoms) or by electrostatic (Coulombic and higher-order) solute-solvent interactions. The latter approach, using the formalism similar to that employed in the description of the solvatochromic effect [24,25], was put forward by Akpe et al. [20].

The present paper is an extension of our earlier research into kinetics and equilibria of aggregation of water-soluble phthalocyanines [17]. We present results of studies of the aggregation of water-soluble sulfonated Pcs with divalent central ions (Cu^{II}, Zn^{II}, Co^{II}). The main purpose of the study reported here was to establish a relation between the electric permittivity of the solutions and the aggregation of the solutes. The equilibrium constants were determined from the absorption spectra measured in solutions of Pcs in binary alcohol–water solvents. For comparison, we also report spectra of tetra-substituted Pcs containing three- and tetravalent central ions (Al(OH)PcS$_4$ and Si(OH)$_2$PcS$_4$), in which formation of π-stacked aggregates is made difficult or obstructed by sterical hindrances.

2. Experimental

2.1. Materials

Sodium salt of tetrasulfonated copper phthalocyanine was purchased from Aldrich. Sodium salts of other sulfonated phthalocyanines ([MPc(SO$_3$Na)$_z$ = MPcS$_z$], M standing for the central ion, and z = 1–4), synthesized from respective unsubstituted phthalocyanines (MPc) according to the procedure described in [26,27], were obtained from Dr J. Rakušan and Dr M. Karásková (Res. Institute for Organic Syntheses, Pardubice-Rybitvi). The compositions of the samples, determined as described in [27], are listed in Table 1.

The procedure of preparing the solutions used in the experiments reported in this papers was as follows. "Mother solution" of a given MPcS$_z$ was obtained by dissolving a determined amount (typically 0.2–0.3 mg, mass determined to within 0.01 mg) of the solid phthalocyanine in 10 cm^3 of pure air-saturated water. The

Table 1
Compositions of the phthalocyanine samples under study.

Phthalocyanine	Composition/purity (wt. %)
ZnPcS$_4$	99.5%
CuPcS$_4$	85%
CuPcS$_{1-3}$	14% CuPcS$_1$
	59% CuPcS$_2$
	26% CuPcS$_3$
CoPcS$_{3-4}$	48% CoPcS$_3$
	47% CoPcS$_4$
Al(OH)PcS$_4$	98%
Si(OH)$_2$PcS$_4$	92% Si(OH)$_2$PcS$_4$
	7% Si(OH)$_2$PcS$_3$

solution used in the spectroscopic measurements (hereafter referred to as "final solution") was then prepared by diluting 0.2 cm^3 of the mother solution with 3 cm^3 of a solvent consisting of pure water or pure alcohol (methanol (MeOH) or ethanol (EtOH); in the studies of CuPcS$_4$, we also occasionally employed glycerine (Gly)), or else in a binary water–alcohol solution. The volume fractions of the alcohols in the final solutions so obtained varied from 0 to 0.94 (the latter ones will be hereafter referred to as 'alcoholic solutions'). By varying the compositions of the solvents we varied their electric permittivities, data published in [28] being used for calibration. The procedure employed allowed us to maintain constant total concentrations (c_{tot}) of Pcs (typically of the order of 10^{-6} M^1) in the final solutions used in a given series of experiments. The concentrations of monomers and dimers were determined from the spectroscopic measurements as will be described in Section 3.2.

2.2. Spectral measurements

Measurements of UV–vis absorption and fluorescence spectra of MPcS$_z$ in solutions were carried out using Shimadzu UV-2101 PC spectrometer and Hitachi F-4500 fluorescence spectrophotometer, respectively. The spectra were measured at ambient temperature.

The fluorescence quantum yields of all phthalocyanines in solutions were measured in reference to a standard sample whose quantum yield had been previously determined by absolute measurements [29]. We employed the procedure recommended in [30]. The quantum yields of the samples under investigation (Φ_s) were calculated from the equation:

$$\Phi_s = \frac{w_s n_{ref}^2 A_{ref}}{w_{ref} n_s^2 A_s} \Phi_{ref} \tag{1}$$

in which Φ_{ref} is the fluorescence quantum yield of the reference sample; n, w, and A stand for the refractive index, the area under the emission spectrum and the absorbance at the excitation wavelength, and the subscripts s and ref refer to the measured and to the reference samples, respectively. We used solution of ZnPc in (toluene + 1% pyridine) as the reference (Φ_{ref} = 0.3) [31]. All measurements were carried out at ambient temperature.

3. Results

3.1. UV–vis absorption spectra

A typical absorption spectrum of the alcoholic solution of a sulfonated phthalocyanine is shown in Fig. 1b. The example shown in the figure is the spectrum of ZnPcS$_4$ but, apart from CoPcS$_{3-4}$

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^{1} M ≡ mol dm^{-3}; this abbreviation will be used throughout the text.
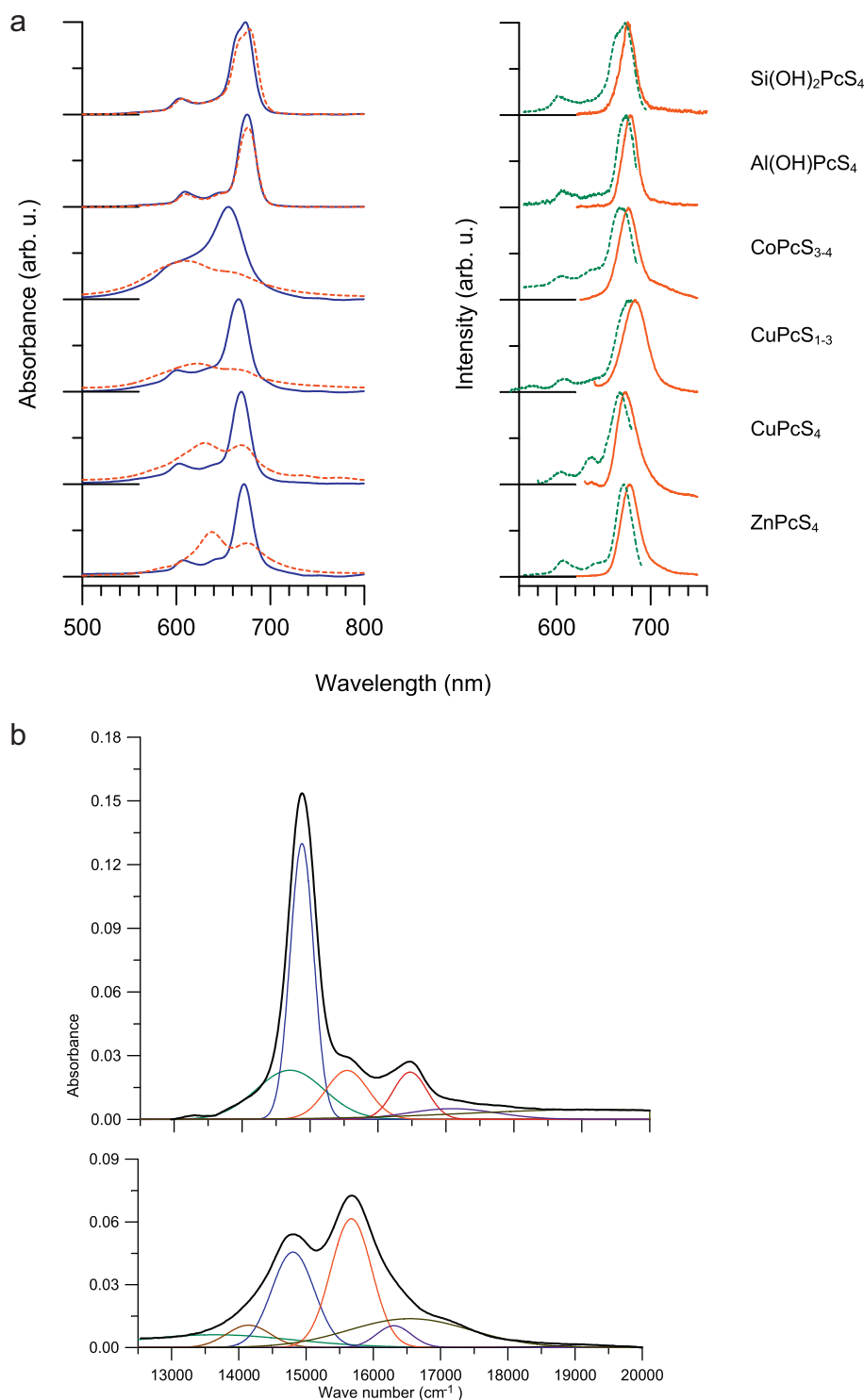
Fig. 2. Spectra of solutions of the sulfonated phthalocyanines in the spectral range of the Q band. (a) Left panel: absorption spectra of alcoholic and aqueous solutions of the phthalocyanines under study (full lines and dashed lines, respectively). Right panel: fluorescence emission and fluorescence excitation spectra (full lines and dashed lines, respectively). (b) Deconvolution of the spectra of alcoholic and aqueous solutions of ZnPcS$_4$ (upper and lower spectrum, respectively). The absorbances of the spectra displayed in the left panel of (a) have been normalized to the heights of the monomer peaks in alcoholic solutions, the spectra in the right panel have been normalized to the respective peak values.

(vide infra), the spectra of the alcoholic solutions of other phthalocyanines under study do not exhibit any qualitative differences. The spectra consist of two main features: Soret (B) band centred around 350 nm and Q band around 670 nm. In the forthcoming analysis, we will concentrate on the spectral range of the Q band. The difference in the positions and shapes of the bands in absorption spectra of

CoPcS$_{3-4}$ as compared with other Pcs under study will be discussed later.

Absorption, fluorescence emission and fluorescence excitation spectra of the Pcs under study in the spectral range of the Q band are shown in Fig. 2a. The main feature in the absorption spectra of the alcoholic solutions of all Pcs is a prominent band peaking

at 670–675 nm, due to the electronic absorption of the monomer molecules (cf. Fig. 2a). This peak is accompanied by a weaker band observed at ca. 603–610 nm. Additional weak and ill-defined features can also be distinguished at ca. 625–640 nm.

Apart from small differences in the positions of the principal bands resulting from differences in the nature of central ions, the exact positions depend also on the number of the sulfonate groups in the molecule. The latter difference, however, is not large; consequently, the absorption spectra of mixtures of Pcs sulfonated to a different degree differ from those of pure Pcs mainly in the widths of the bands (see Fig. 2a and Table 2).

A characteristic feature of absorption spectra of Pcs containing divalent central metals is the change of the shape of the spectra on changing the composition of the solvent from alcoholic to aqueous, and appearance of well discernible bands due to presence of dimers and/or higher aggregates (cf. Fig. 2b). These bands are situated on the high energy sides of the monomer bands (at ca. 640 nm), overlapping with weak vibrational satellite bands; their intensities depend on the electric permittivity of the solvent. Additionally, broad and ill-defined features appear on the low-energy side of the monomer band (around and above 700 nm). These changes are accompanied by a decrease of the fluorescence intensity: the emission of aqueous solutions of phthalocyanines of the divalent metals could not be recorded.

It is important to note that such changes have not been observed in the spectra of Al(OH)PcS$_4$ and Si(OH)$_2$PcS$_4$, i.e., in Pcs containing one or two OH groups attached to the central ion (cf. Fig. 2a).

The main parameters characterizing the spectra of the phthalocyanines under study are collected in Table 2.

Fluorescence emission and excitation spectra of the phthalocyanines under study could be reliably measured only in alcohol-rich solvents (cf. Fig. 2a). In alcoholic solutions, the fluorescence quantum yield was found dependent on the nature of the central metal (see Table 3), ranging from 0.74 in Al(OH)PcS$_4$ to ca. 0.03 in CuPcS$_4$ and 0.015 in CuPcS$_{1-3}$, and to less than 0.01 in CoPcS$_{3-4}$. Moreover, even in ZnPcS$_4$, exhibiting reasonable fluorescence quantum yield in alcoholic solutions, the emission intensity decreases rapidly in solutions whose relative electric permittivities exceed 60 (i.e., in solutions in which the weight fraction of water exceeds 0.5 in MeOH/H$_2$O or 0.7 in EtOH/H$_2$O mixed solvents). The changes in the emission intensities scale with changes in the height of the monomer peak in the absorption spectrum (cf. Fig. 3a), the scaling being a natural consequence of the non-fluorescent nature of the dimers. This dependency will be discussed in the next section; unfortunately, similar dependencies could not be established in solutions of other phthalocyanines, due to the low fluorescence quantum yields.

With a notable exception of CoPcS$_{3-4}$, the shapes of the absorption spectra and positions of the absorption peaks are well reproduced in the fluorescence excitation spectra (cf. Fig. 2a and Table 2). In the absorption spectrum of CoPcS$_{3-4}$, the band attributed to monomers peaks at 659 nm (15,175 cm^{-1}), i.e., at the wave number ca. 200–300 cm^{-1} higher than the corresponding bands in other phthalocyanines under study. Moreover, its half width is exceptionally large. It is interesting to note that these features are not reproduced in the excitation spectrum: both, the position of the maximum and the half width do not deviate from the respective values determined for other Pcs. The difference seems to indicate that aggregates (predominantly dimers) are present in noticeable quantities already in diluted alcoholic solutions of CoPcS$_{3-4}$, and higher aggregates prevail in aqueous solutions. The presence of (non-emitting) aggregates probably accounts also for the very low intensity of emission of alcoholic solutions of CuPcS$_{1-3}$.

Table 2
Positions of the principal features appearing in the spectral region of the Q band of solutions of the phthalocyanines under study (Pc concentrations were of the order of 10^{-6} M).

| Phthalocyanine | Absorption spectra | | | | | | | | | | Excitation spectra[a] | | |
| | Monomer band[b] | | | Side band[c] | | | Dimer band[b] | | | | | |
	Wavelength (nm)	Wave number (cm^{-1})	Half width (cm^{-1})	Wavelength (nm)	Wave number (cm^{-1})	Assignment (cm^{-1})	Wavelength (nm)	Wave number (cm^{-1})	Wavelength (nm)	Wave number (cm^{-1})	Half width (cm^{-1})
ZnPcS$_4$	674	14837	485	609	16420	0–0 + 1583	638	15674	671	14905	460
CuPcS$_4$	672	14881	510	606	16502	0–0 + 1621	631	15848	668[c]	14970[c]	575[c]
CuPcS$_{1-3}$	670	14925	560	603	16584	0–0 + 1659	626	15974	676	14793	690
CoPcS$_{3-4}$	659	15175	1200	Hidden			619[d]	16155	668	14970	655
Al(OH)PcS$_4$	676	14793	465	610	16393	0–0 + 1600	–	–	673	14859	460
Si(OH)$_2$PcS$_4$	675	14815	610	605	16529	0–0 + 1714	–	–	673	14859	615

[a] Main band in alcoholic solution.
[b] Aqueous solution.
[c] DMF.
[d] CoPcS$_{3-4}$: the band is probably due to a higher aggregate (see the text).

Table 3
Fluorescence quantum yields (Φ_F) in ethanolic solutions of phthalocyanines under study.

Phthalocyanine	Φ_F
ZnPcS$_4$	0.31
CuPcS$_4$	0.03
CuPcS$_{1-3}$	0.015
CoPcS$_{3-4}$	Not determined
Al(OH)PcS$_4$	0.74
Si(OH)$_2$PcS$_4$	0.54

3.2. Dimerization equilibria

As was already mentioned in the preceding sub-section, the shapes of the absorption spectra were found dependent on the composition of solvents: the intensities of the bands due to the absorption of monomeric Pcs decrease on passing from alcoholic to aqueous solutions whereas the features attributed to the absorption of aggregates (primarily dimers) gain intensity, the changes being particularly pronounced for water-rich solvents as is shown in Fig. 3a and b on the examples of ZnPcS$_4$ and CuPcS$_{1-3}$. This
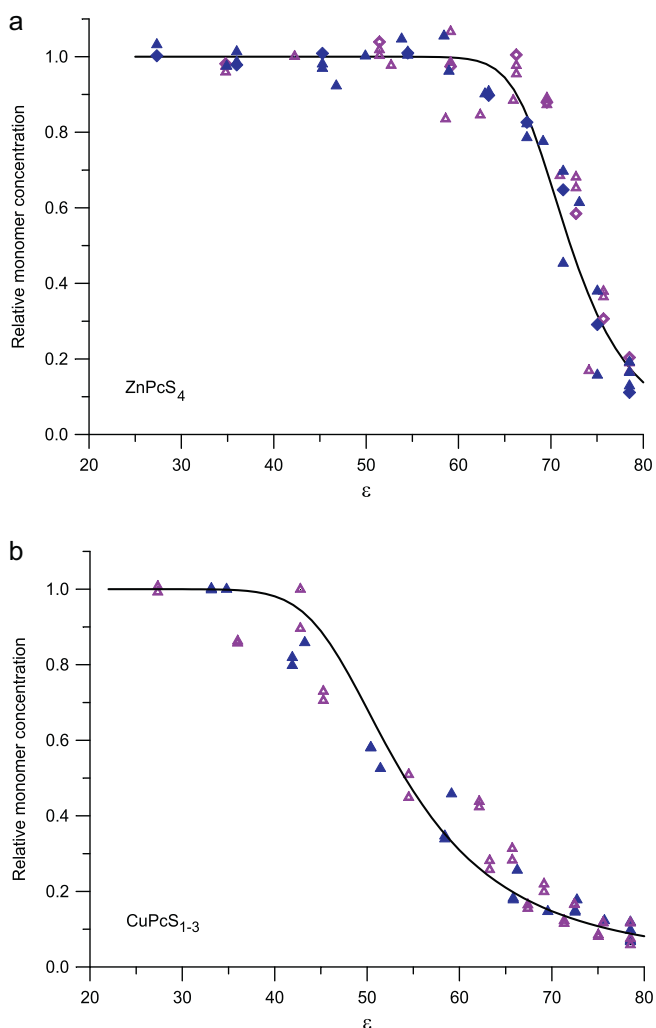

Fig. 4. Dependence on the electric permittivity of the equilibrium constant of dimerization of phthalocyanines under study. Different symbols represent different organic molecules in the binary solvents. The straight lines are fits to the experimental data with Eq. (3).

behavior was exploited to determine the equilibrium constants of dimerization of the Pcs under study in function of the electric permittivity of the solvent.

The equilibrium constants of dimerization (K_D) were determined for each solution from the equation:

$$K_D = \frac{c_D \times c^0}{c_M^2} \qquad (2)$$

where c_D and c_M stand for the concentrations of dimers and monomers, respectively (expressed in M), and c^0 is the standard concentration ($c^0 = 1$ M).

The concentrations of monomers and dimers were determined from the absorbances of respective Pcs in their Q bands in the following way: assuming the concentrations of the dimers negligibly small in the alcoholic solutions and knowing the total concentration of a given Pc (see Section 2.1), we could determine the molar absorbance of its monomeric form from the Lambert–Beer law. The molar absorbance so obtained was then exploited in determining concentrations of monomers in all solutions of the phthalocyanine. The concentrations of dimers were determined from the differences between the total concentrations and the concentrations of the monomers: $c_D = (1/2)(c_{tot} - c_M)$.

It follows from Fig. 3 that the relative error on determining the concentrations of monomers (and hence the concentrations of dimers) was as high as ca. 20%. Consequently, the dimerization constants could only be calculated with an acceptable accuracy over a limited range of compositions of the binary solvents in which the concentrations of monomers and dimers were not much different. The results, shown in Fig. 4, demonstrate that the dimerization constants depend on the electric permittivity of the solvents, following the relation:

$$\ln \quad K_D = A - \frac{B}{\varepsilon} \qquad (3)$$

where A and B are parameters independent of ε. It should be noted that, to within the experimental error, the degree of aggregation seems not to depend on the alcohol used.

4. Discussion

4.1. The model

The dimerization of sulfonated phthalocyanine anions can be described in terms of interaction between assemblies of bonded

Fig. 3. Relative concentrations of Pc monomers in function of the relative electric permittivities of binary solvents: (a) ZnPcS$_4$; (b) CuPcS$_{1-3}$. Open symbols: water–methanol, closed symbols: water–ethanol. Triangles: monomer concentrations determined from the absorption spectra, diamonds: emission intensities normalized to the values determined in the alcoholic solutions. The continuous lines are the relative monomer concentrations calculated from the model described in Section 4.1.
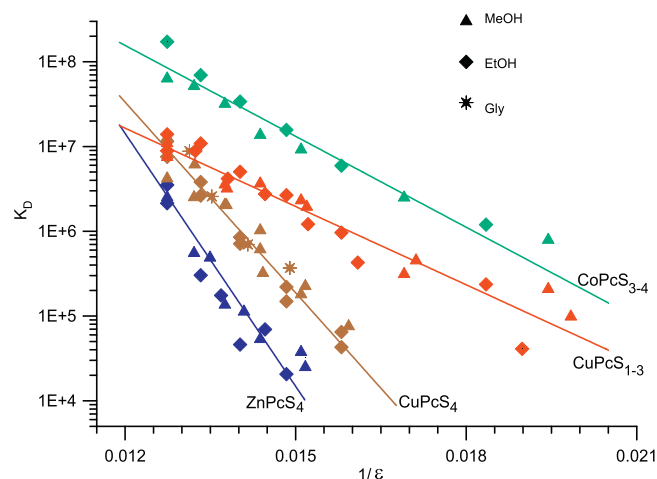
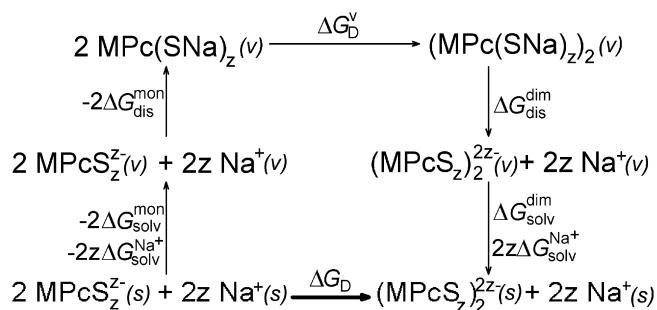$$2\,MPc(SNa)_z\,(v) \xrightarrow{\Delta G_D^v} (MPc(SNa)_z)_2\,(v)$$

Fig. 5. The thermodynamic cycle for the calculation of the dimerization equilibrium. The chemical symbol of sodium has been added to the abbreviated formulae of the monomer and dimer Pcs employed throughout the text. The superscripts mon and 'dim' refer to monomer and dimer, respectively, the subscripts 'dis', 'solv' and 'D' – to dissociation, solvation and dimerization, respectively, the symbols (v) and (s) denote vacuum and solution, respectively.

atoms (representing molecules) and charges, dispersed in a continuous medium (solvent) of a relative electric permittivity (dielectric constant) ε. In this sense, the description of the interaction energy would be equivalent to using a combination of the submolecule treatment [32] (or, in the limit, of the atom–atom potentials [33]) and the generalized Born approach (e.g., [34,35]). In our approach, aiming at derivation of simple analytical equations describing the results reported in the preceding section on a semi-quantitative level, the sulfonated phthalocyanine anions are mimicked by charged spherical objects of charge $-ze$ and radius a, dispersed in a solvent of a relative electric permittivity ε. The Gibbs free energy of dimerization (ΔG_D), taking into account changes in solvation of the monomers and dimers, can be calculated from the thermodynamic cycle schematically shown in Fig. 5.

It follows from the scheme that:

$$\Delta G_D = \Delta G_D^V + (\Delta G_{dis}^{dim} - 2\Delta G_{dis}^{mon}) + (\Delta G_{solv}^{dim} - 2\Delta G_{solv}^{mon}) \tag{4}$$

where ΔG_D^V is the Gibbs free energy of dimerization of two neutral $MPc(SNa)_z$ molecules *in vacuo*, ΔG_{dis}^{mon} and ΔG_{dis}^{dim} stand for the dissociation energies of monomers and dimers *in vacuo*, and ΔG_{solv}^{mon} and ΔG_{solv}^{dim} are the solvation energies of monomers and dimers, respectively. The first right hand term can be derived from the expression describing interaction between a pair of neutral molecular entities: we will adopt the Lennard–Jones potential:

$$E(r) = E_0 \left[2\left(\frac{2a}{r}\right)^6 - \left(\frac{2a}{r}\right)^{12} \right] \tag{5}$$

where r is the distance between the centers of the spheres and E_0 is the interaction energy of uncharged "molecules" at the equilibrium distance $2a$ ($E_0 < 0$). In the present model, the dimerization is a process of bringing two non-interacting spherical particles ('monomers') to the distance $2a$. The work required for such a process (i.e., change in the Gibbs free energy) *in vacuo*, calculated for 1 mol of the dimers, is given by the equation:

$$\Delta G_D^V = U_0 - T\Delta S_D \tag{6}$$

where $U_0 = N_0 E_0$, N_0 being the Avogadro number, and ΔS_D represents changes in entropy due to processes not accounted for in the present model.

The dissociation energies of neutral monomer and dimer molecules *in vacuo* can be understood to a first approximation as the work of separation of cations from large molecular anions against the Coulombic attraction forces. One should note, however, that the difference ($\Delta G_{dis}^{dim} - 2\Delta G_{dis}^{mon}$), irrespective of its value, is independent of ε. The contribution to ΔG_D associated with changes in the

solvation during the dimerization can be estimated employing the classical equation given by Born [36]:

$$\Delta G_{solv}^i = -\frac{N_0 z_i^2 e^2}{8\pi\varepsilon_0 r_i}\left(1 - \frac{1}{\varepsilon}\right) \quad (i = mon, dim) \tag{7}$$

where r_i stand for effective radii of the monomer (mon) or dimer (dim). Inserting Eqs. (6) and (7) into (4), one obtains:

$$\Delta G_D = U_0 - T\Delta S_D + \Delta(\Delta G_{dis}) - \frac{N_0 e^2 z^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{\varepsilon}\right) \tag{8}$$

where $\Delta(\Delta G_{dis}) = (\Delta G_{dis}^{dim} - 2\Delta G_{dis}^{mon})$, $r_0^{-1} = 2r_{dim}^{-1} - a^{-1}$. The expression for the equilibrium constant of dimerization thus reads:

$$\ln K_D = -\frac{\Delta G_D}{RT} = -\left(\frac{U_0}{RT} - \frac{\Delta S_D}{R} + \frac{\Delta(\Delta G_{dis})}{RT} + \frac{N_0 z^2 e^2}{4\pi\varepsilon_0 r_0 RT}\right) - \frac{N_0 z^2 e^2}{4\pi\varepsilon_0 r_0 RT} \times \frac{1}{\varepsilon} \tag{9}$$

A comparison of Eqs. (10a), (10b) and (3) yields:

$$A = -\left(\frac{U_0}{RT} + \frac{\Delta S_D}{R} + \frac{\Delta(\Delta G_{dis})}{RT} + \chi\frac{z^2}{r_0 T}\right) \tag{10a}$$

$$B = \chi\frac{z^2}{r_0 T} \tag{10b}$$

where

$$\chi = \frac{N_0 e^2}{4\pi\varepsilon_0 R} = 1.725 \cdot 10^{-5} \quad \text{m} \cdot \text{K} \tag{11}$$

The following conclusions can be drawn from the analysis of the above equations:

(i) The dimerization constants of the Pcs with divalent central ions should depend on the electric permittivities but not on the compositions of the solvents.

(ii) One should expect a linear dependence of $\log K_D$ on $1/\varepsilon$.

(iii) The slopes of the $\log K_D$ vs. $1/\varepsilon$ dependences should depend on z, i.e., on the number of sulfonate groups, scaling with z^2.

(iv) The parameter r_0 is expected to be of the order of molecular dimensions. Moreover, values of the parameter should be similar for sulfonated phthalocyanines complexed with various divalent central atoms.

The values of the parameters A and B calculated from the slopes of experimental K_D vs. $1/\varepsilon$ dependencies (see Fig. 4) are collected in Table 4. These values can now be used to calculate the dependencies of the concentrations of monomer molecules on the electric permittivity of the solutions. Exemplary results are shown in Fig. 3a (for $ZnPcS_4$) and b (for $CuPcS_{1-3}$): the continuous lines on the figures have been calculated taking the values listed in Table 4.

The results obtained for $ZnPcS_4$ can be employed to determine the parameter r_0. Use of Eq. (10b) and the parameters of Table 4 yields $r_0 = 0.4$ nm, reasonably close to the distance between the molecular planes in phthalocyanine crystals amounting to 0.34 nm [37]. Keeping in mind severe simplifications introduced in the model, the agreement may be assessed as very good.

4.2. Aggregation in solutions of phthalocyanines with mixed degree of sulfonation

It was already mentioned in the preceding section that the spectra of the phthalocyanines under study weakly depend on the degree of sulfonation and, to a first approximation, absorption spectra of mixtures of differently sulfonated Pcs differ from those of pure compounds mainly in half-widths of the bands. Consequently, formation of dimers of differently charged Pc ions can be described

Table 4
Parameters extracted from the fit with Eq. (3) of the experimental results from Fig. 4.

Sample	Molar fractions of the sulfonated Pcs	A	B	z_{eff} calculated from B with $r_0 = 0.4$ nm	z_{eff} calculated from Eq. (12)
ZnPcS$_4$	$x_{ZnPcS_1} + x_{ZnPcS_2} + x_{ZnPcS_3} = 0.01$ $x_{ZnPcS_4} = 0.99$	44.0	2291	4.0[a]	4.0
CuPcS$_4$	$x_{CuPcS_1} + x_{CuPcS_2} + x_{CuPcS_3} = 0.16$ $x_{CuPcS_4} = 0.84$	38.1	1727	3.5	3.5–3.8[b]
CuPcS$_{1-3}$	$x_{CuPcS_1} = 0.17$ $x_{CuPcS_2} = 0.60$ $x_{CuPcS_3} = 0.23$	25.1	709	2.2	2.1
CoPcS$_{3-4}$	$x_{CoPcS_1} + x_{CoPcS_2} = 0.06$ $x_{CoPcS_3} = 0.50$ $x_{CoPcS_4} = 0.44$	28.7	823	2.4	3.3–3.4[b]

[a] Calibrating value, allowing for determination of r_0.
[b] Depending on the degree of sulfonation.

within the model as the aggregation of two charged species, each with a charge z_{eff}. If the value of r_0 is known, then z_{eff} can be calculated from Eq. (10b), taking the value of B from Table 4. On the other hand, z_{eff} can be calculated if the composition of the sample is known. Assuming that encounters of Pc ions take place at random, one may easily show that:

$$z_{eff}^2 = \sum_{i=1}^{4} \left[x_i z_i \left(\sum_{j=1}^{4} x_j z_j \right) \right] \tag{12}$$

where x_i are molar fractions of differently sulfonated phthalocyanines and z_i are their charges. Values of z_{eff} are compared in Table 4. For CuPcS$_4$ and CuPcS$_{1-3}$ the agreement beween z_{eff} obtained from both sources is reasonable. In the case of CoPcS$_{3-4}$, however, the two methods yield completely different results. The discrepancy can be rationalized taking into account the fact that the model describes the formation of a dimer from two monomer molecules and implicitly assumes that the dimerization is the only equilibrium process in the system. The spectroscopic results described in the preceding section clearly demonstrate that this is not the case for CoPcS$_{3-4}$ where dimers are present in noticeable amounts already in alcoholic solutions and the shift of the bands indicates that higher aggregates are formed in aqueous solutions.

4.3. Comparison with published results

It would be instructive to compare the results obtained in the research described in this paper with those reported earlier in the literature. Schelly et al. [8] determined the dimerization constants in aqueous solutions of CoPcS$_4$ for 311 K < T < 331 K. Extrapolation of their results to the room temperature yields $K_{dim} =$ ca. 3×10^6, slightly above the result obtained by us for the sample with a lower degree of sulfonation. Bernauer and Fallab [7] gave the values of dimerization constants in aqueous solutions of H$_2$PcS$_4$, CoPcS$_4$, CuPcS$_4$ and ZnPcS$_4$ at temperatures close to 333 K. The value reported for CoPcS$_4$ is close to that given in [8], whereas the dimerization constant of ZnPcS$_4$ at 331 K amounts to ca. 10^6, about 3–4 times less than the the value obtained in this work at 293 K. Brożek-Płuska et al. [18,19] reported the room temperature values of the dimerization constants in solutions in DMSO and water of MgPcS$_4$ and ZnPcS$_4$. The constant in the aqueous solution of ZnPcS$_4$ is ca 3–5 times lower than that reported in this paper. What is more important, however, the parameters ($d \ln K_{dim}/d\varepsilon^{-1}$) (corresponding to B in Eq. (3)) estimated from the reported values of K_{dim} in water and in DMSO, amount to ca. 830 for ZnPcS$_4$ and ca. 200 for MgPcS$_3$, i.e., are much lower than expected from our model for tetra-sulfonated Pcs. This disagreement may indicate that specific interactions, neglected in the model put forward in the present paper, do play an important role in the aggregation of soluble Pcs.

In our opinion, however, the disagreement can be attributed to either of two factors: (i) the constants were determined from measurements performed for concentrations up to 10^{-4} M, where the presence of aggregates higher than dimers cannot be neglected, (ii) the degree of sulfonation of the materials used was lower than 4. Assuming that the former factor is not the primary reason for the discrepancy, the slopes deduced from the results reported in [18,19] would correspond to z_{eff} close to 2 in zinc phthalocyanine, and to ca. 1 in magnesium phthalocyanine.

5. Concluding remarks

We have studied the process of aggregation of soluble phthalocyanines. Our results provide quantitative estimates of the aggregation constants of soluble phthalocyanines with divalent central metals in aqueous solutions. The equilibrium constants of dimerization were found dependent on the electrical permittivity of the solvent and on the degree of sulfonation (i.e., on the charge on the phthalocyanine anions). From the point of view of the applicability of these phthalocyanines in medicine, formation of aggregates is an unwanted process as the excitation energy of such aggregates is effectively dissipated via radiationless channels [9]. A comparison of the behavior of Pcs of divalent atoms with those of tri- and tetravalent atoms shows that the dimerization is far less efficient in phthalocyanines in which the aggregation is hindered by, e.g., functional groups attached to the central atoms or by bulky substituents attached to periferial rings. Our earlier studies [17] of the behavior of Al(OH)PcS$_i$ have shown that the room-temperature dimerization constants in aqueous solutions are of the order of 10^4 hence monomeric species exist even in relatively concentrated solutions. For example, the association degree at c ~ 10^{-3} M is approximately equal to 0.8, i.e., the concentration of the monomeric Al(OH)PcS$_i$ in such solutions still amounts to ca. 2×10^{-4} M.

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