ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 11, pp. 850–856. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © Yu.I. Churakhina, Yu.B. Ivanova, O.V. Maltzeva, N.Zh. Mamardashvili, 2009, published in Koordinatsionnaya Khimiya, 2009, Vol. 35, No. 11, pp. 860–866.

Complexation and Basic Properties of Polyethylene Oxide–Substituted Porphyrins

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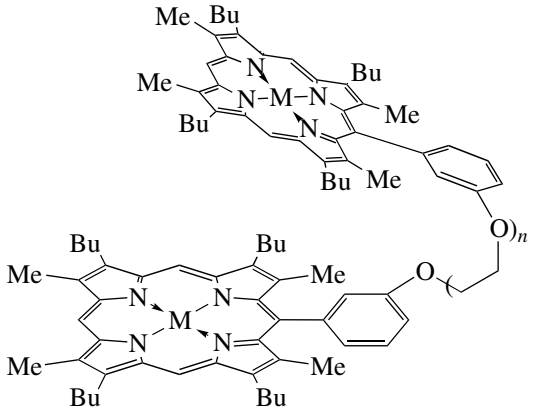
Received March 25, 2009

Abstract—Basic properties of bis[5-(3-oxyphenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrinyl]-3,6,9-trioxyundecane-1,11 and bis[5-(3-oxyphenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrinyl]-3,6,9,12-tetraoxytetradecane-1,14 were studied spectrophotometrically in an ethanol–sulfuric acid system; the influence of the basicity of the inner cycle nitrogen atom on the complexation properties of these polyethylene oxide–substituted porphyrins towards zinc cation in ethanol was considered.

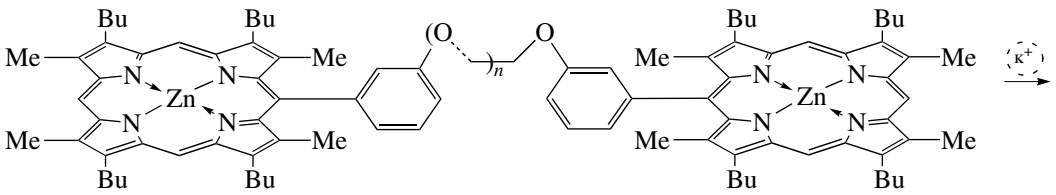
DOI: 10.1134/S1070328409110104

Recently, among diverse receptor–substrate-type interactions, special attention has been drawn to the processes of tetrapyrrole chromophore complexation with metal cations of different nature [1, 2]. First of all, the topicality of the problem stems from the need to identify and separate biologically active substrates. From this point of view, tetrapyrrole chromophores modified with polyethylene oxide fragments are of undoubted interest. Tetrapyrrole chromophore in these supramolecules could serve as primary transmitters of the analytical signal in the optical response of the receptor. Polyethylene oxide fragments, capable of binding alkali metal cations, could be used as "building blocks" fixing the reaction centers of a macroheterocycle in a specific orientation relative to each other:

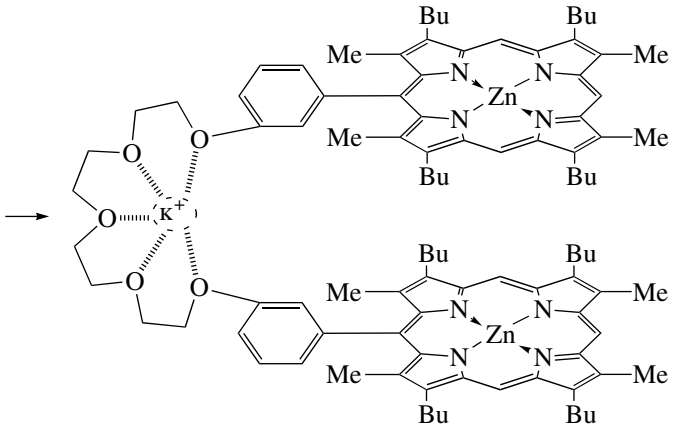


M = Zn (**I**, **II**), H_2 (**III**, **IV**); n = 4 (**I**, **III**), 5 (**II**, **IV**)

Earlier [3], we reported on research of the complexation ability of polyethylene oxide fragments of bisporphyrinates **I**, **II** with respect to potassium cation in toluene-methanol (5:1) mixture. It was found that due to the geometric match between the tetraethylene oxide complexing cavity and the dimensions of the substrate, **I** is able to bind K^+, forming the complex **V**:



(n = 4)
(**I**)



(**V**)

The conformational changes accompanying the complexation result in an approximation of the porphyrin fragments of the dimer, easily detected by EAS and ^{1}H NMR spectra.

EAS of **V** demonstrates a hypsochromic shift, broadening, and decrease in intensity of the absorption bands relative to those of **I**, i.e., all the typical features of excitron interactions of π-electron systems of closely positioned and oriented face-to-face tetrapyrrole chromophores. The mutual shielding effect of ring currents of neighboring tetrapyrrole macrocycles is also evident from the downfield shift of porphyrin proton signals in the ^{1}H NMR spectrum of **V** relative to the corresponding proton signals of **I**. The stability constant (K_y) of this complex (0.081×10^6 l/mol) [3] was determined spectrophotometrically based on the data for two wavelengths (decreasing and increasing).

The goal of the present work is to study the complexation ability of tetrapyrrole fragments of supramolecules bis[5-(3-oxyphenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrinyl]-3,6,9-trioxyundecane-1,11 (**III**) and bis[5-(3-oxyphenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-porphyrinyl]-3,6,9,12-tetraoxytetradecane-1,14 (**IV**) towards zinc cation in ethanol. The ability of tetrapyrrole macrocycles to coordinate metal ions depends on the basicity of their inner cycle nitrogen atoms; thus, prior to the complexation studies, we characterized the basicity of compounds **III** and **IV** in an ethanol–sulfuric acid mixture.

EXPERIMENTAL

Porphyrins **I**–**IV** were obtained as described in [3]. EAS were recorded on a Cary 100 spectrophotometer. The reaction was monitored with TLC on Sulfol UV-254 plates with a 3 : 1 trichloroethylene-hexane mixture as an eluent. Individual compounds were isolated by column chromatography on neutral aluminum oxide. The eluent consisted of a mixture of trichloroethylene and hexane. Organic solvents were purified as described in [4].

Spectrophotometric titration of **III** and **IV** with sulfuric acid in ethanol was carried out on a Cary 100 spectrophotometer (Varian Inc.). The experimental procedure and data processing were as presented in detail in [5, 6]; the error in determining the corresponding constants was ±(3–5)%.

The kinetics of the complexation reactions of **III** and **IV** with zinc acetate was also monitored spectrophotometrically. Kinetic experiments were performed in thermostated cells with temperature fluctuations that did not exceed ±0.1 K. In all cases, the spectra of the reacting systems demonstrated the presence of a clear isosbestic point. The experiment protocol and data processing were as presented in detail in [7]; the error in determining the corresponding constants was ±(3–5)%.

Table 1 gives the parameters of EAS measurements of bisporphyrinate ligands **III** and **IV**, their di- and tetracationic forms in C_2H_5OH–H_2SO_4, and zinc bisporphyrinates **I** and **II** in ethanol. The values of the wavelengths of isosbestic points of processes (4), (5), and (10) are summarized in Table. 2.

RESULTS AND DISCUSSION

In the absence of specific interactions, H_2P porphyrins in the H_2P–C_2H_5OH–H_2SO_4 system are protonated at tertiary nitrogen atoms, forming mono- (H_3P^+) and dicationic (H_4P^{2+}) particles (Eqs. 1 and 2), which exist in certain concentration ranges depending on the set of initial reagents [8, 9]. The major ionization usually proceeds in two steps, and the second proton, naturally, attaches with greater difficulty than the first:

$$H_2P + H^+ \overset{K_{b1}}{\rightleftharpoons} H_3P^+, \quad (1)$$

$$H_3P^+ + H^+ \overset{K_{b2}}{\rightleftharpoons} H_4P^{2+}. \quad (2)$$

Bisporphyrins **III** and **IV** (H_4P) in acidic media exist in two forms, which have a different position and

intensity of the absorption bands maxima in the EAS. In multicenter bases, where several inner pyrrole nitrogen atoms are able to participate in acid–base interactions, it is important to establish the number and status of electron centers.

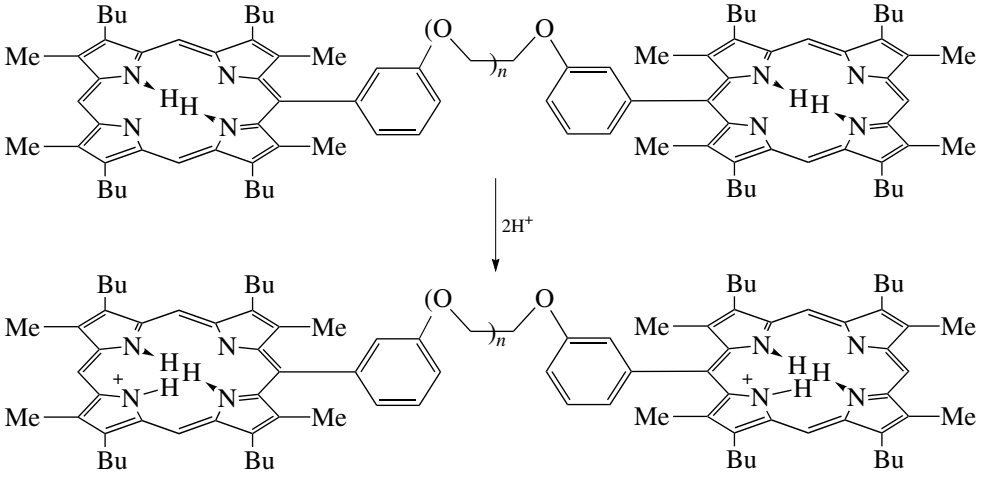
A spectrophotometric titration study of ionization of **III** in ethanol–sulfuric acid systems demonstrated that protonation of tetrapyrrole macrocycles (with an increase in the acid concentration in solution) is accompanied by the consecutive formation of two families of spectroscopic curves with corresponding isosbestic points (Fig. 1).

Ionization of H_4P in an acid concentration range of 0–6.4×10^{-4} mol/l is characterized by the presence of only one family of spectral curves with a specific set of isosbestic points in the EAS (Table 2, Fig. 2a).

Analysis of the literature data [10–14] and our own earlier results [5–6] suggest that, in the above-mentioned concentration range of sulfuric acid, the acid–base interactions in the H_4P–H_2SO_4 system could be described by the equation

$$H_4P + 2H^+ \overset{K_{b1}}{\rightleftharpoons} H_6P^{2+} \quad (3)$$

and represented as

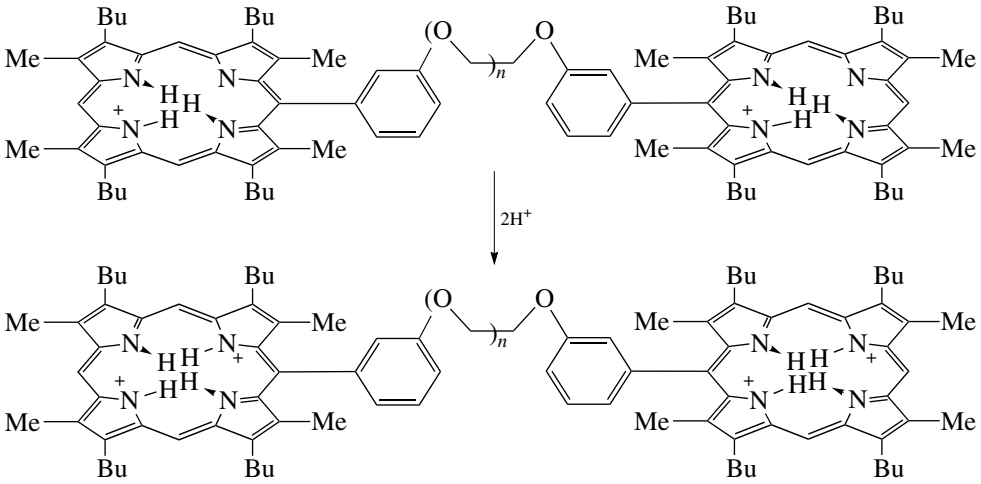


Further increase in the acid concentration results in further protonaton of the macrocycles, seen as the consecutive formation of another family of the spectra with a specific set of isosbestic points in the EAS (Fig. 2b).

Investigation of H_6P^{2+} ionization in a range of sulfuric acid concentrations of 6.4×10^{-4}–2.5×10^{-3} mol/l revealed the presence of another family of spectral curves with a specific set of isosbestic points in the EAS (Table 2, Fig. 2b); i.e., the acid–base interactions H_6P^{2+}–H_2SO_4 in this acid concentration range could be described by the equation

$$H_6P^{2+} + 2H^+ \overset{K_{b2}}{\rightleftharpoons} H_8P^{4+} \quad (4)$$

and represented as



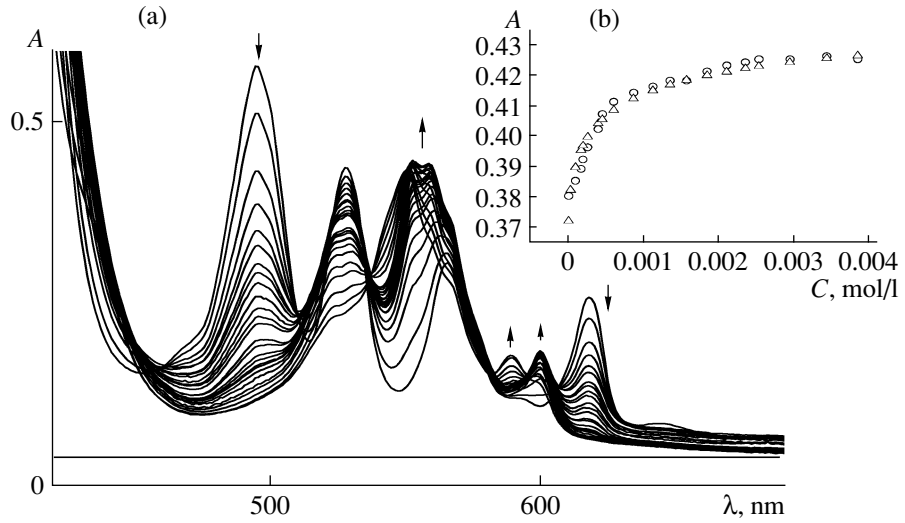


Fig. 1. Changes in EAS of **III** (1.0×10^{-5} mol/l) in the ethanol–sulfuric acid system $c_{H_2SO_4} = 0–2.5 \times 10^{-3}$ mol/l (a); titration curve at analytical wavelength λ == 549 nm (b).

The observed spectral changes (Figs. 1, 2) allow us to calculate the protonation constants of H_6P^{2+} and H_8P^{4+} according to the following equations:

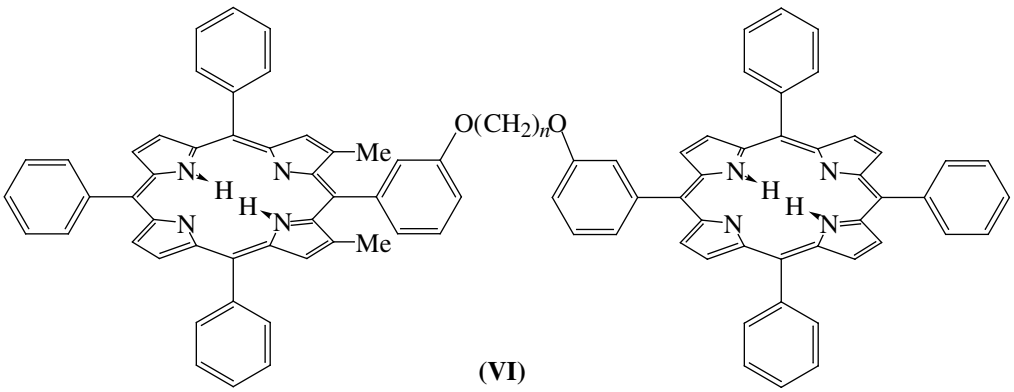
$$pK_{b_1} = H_0 + \log(c_{H_6P^{2+}}/c_{H_4P}), \quad (5)$$

$$pK_{b_2} = H_0 + \log(c_{H_8P^{4+}}/c_{H_6P^{2+}}). \quad (6)$$

Similar results were obtained for the ionization of bisporphyrin **IV**. Table 3 gives the values of the basicity constants for **III** and **IV**.

According to the reaction mechanism of metal cations coordinated by porphyrins in nonaqueous media [15], formation of metalloporphyrins occurs as a result of bimolecular collision of the porphyrin ligand and solvated salt. The rate of complexation depends, on the one hand, on the strength of N–H bond in the reaction center of porphyrin and, on the other hand, on coordination interactions of metal cation with nitrogen atoms of porphyrin. The influence of these factors may vary depending on the specific conditions of complexation.

In conformationally flexible porphyrin dimers with one bridge connecting macrocycle units, the mutual influence of porphyrin fragments is not apparent. The authors of [16] demonstrated that porphyrin fragments had no mutual influence on the kinetics of the tetraphenylporphyrin dimer with one connecting bridge (**VI**):



(VI)

It was found that interactions of **VI** with *d*-metals result in the successive formation of mono- and binuclear complexes. The complexation reaction is described by a first-order equation relative to porphyrin. The kinetic parameters of the reaction of the metal solvatocomplex with the ligand and its mononuclear complex appear indistinguishable within the experimental error.

We have used a spectrophotometric method to study the kinetics of complexation of porphyrins **III** and **IV** with $ZnAc_2$ in ethanol. Figure 3 illustrates the change in

Table 1. EPS of molecular, di-, and tetracationic forms of bisporphyrin ligands **III** and **IV** in the system $C_2H_5OH–H_2SO_4$ and of zinc bisporphyrinates **I** and **II** in C_2H_5OH at λ_{max}, nm ($\varepsilon \times 10^{-3}$ l/(mol cm))

Compound	λ_1	λ_2	λ_3	λ_4	$c_{H_2SO_4}$, mol/l
III ($n = 4$)					
H_4P	496 (4.28)	528 (4.18)	566 (4.05)	618 (3.99)	0
H_6P^{2+}	496 (3.91)	530 (4.12)	560 (4.20)	600 (3.84)	5×10^{-4}
H_8P^{4+}			551(4.20)	589(3.85)	2.5×10^{-3}
IV ($n = 5$)					
H_4P	495 (4.41)	528 (4.30)	566 (4.15)	618 (4.09)	0
H_6P^{2+}		530 (4.06)	559 (4.17)	600 (3.83)	1.2×10^{-3}
H_8P^{4+}			550 (4.18)	589 (3.86)	1.6×10^{-2}
I	405 (5.27)		535 (4.17)	573 (4.18)	
II	405 (5.29)		536 (4.21)	574 (4.23)	

the absorption spectrum of the reaction system $H_4P–Zn^{2+}$ in the course of their interactions.

Analysis of the literature [16] and our own data suggests that first a mononuclear complex of bisporphyrin (MH_2P) forms,

$$H_4P + MAc_2 \longrightarrow MH_2P + 2HAc, \quad (7)$$

which upon contact with the metal cation becomes a binuclear complex:

$$MH_2P + MAc_2 \longrightarrow M_2P + 2HAc. \quad (8)$$

Since the flexible ether bridge is not able to fix two tetrapyrrole macrocycles relative to each, their mutual influence is minimal. Clear isosbestic points are observed in the spectra of the reaction system of salt–porphyrin (Fig.3). The EAS of the H_4P and M_2P mixture (1 : 1) do not differ from the spectrum of MH_2P.

Table 2. Values of the wavelength of isosbestic points of processes 3, 4, and 9 with bisporphyrins **III** and **IV** in the $C_2H_5OH–H_2SO_4$ system and of zinc bis-porphyrinates **I** and **II** in C_2H_5OH at λ_{max}, nm

Porphyrin (equation)	λ_1	λ_2	λ_3
III (3)	606	511	459
III (4)	595	581	538
IV (3)	606	511	457
IV (4)	596	581	537
I (9)	397	528	583
II (9)	399	531	587

The mutual influence of tetrapyrrole fragments is not apparent in terms of the complexation kinetics. H_4P interaction with zinc acetate is described by the usual kinetic equation for porphyrins, i.e., it has a first order in terms of porphyrin:

$$d[H_2P]/d\tau = -k_v[H_2P][MAc_2]. \quad (9)$$

Additional evidence for this is the linear character of the $\log\ \log(c^0_{H_4P}/c_{H_4P}) = f(\tau)$ dependence (Fig. 3).

The presence of MH_2P in the reaction system of $MAc_2–H_4P$ was confirmed by thin-layer chromatography on silufole (R_f values of 0.77 (M_2P), 0.65 (MH_2P), and 0.45 (H_4P), eluent–toluene). The kinetic parameters characterizing formation of M_2P in $ZnAc_2$ interactions with H_4P or MH_2P are identical within the range of errors. Kinetic measurements were carried out in the presence of a ~100-fold excess of salt relative to the porphyrin ligand; this allowed calculating the complexation rate constant (k_v) from the equations:

$$k_v = k_{ef}/[MAc_2], \quad (10)$$

$$k_{ef} = 1/\tau \ln(A_0 - A_\infty)/(A - A_\infty), \quad (11)$$

where A_0, A_∞, and A are the optical densities of solutions at the beginning and end of the reaction, and at time τ, respectively. The error in determining k_v was ±(3–5)% (Table 3).

Thus, the basic properties of bisporphyrins with different lengths of the polyethylene oxide linking bridge were studied spectrophotometrically in an ethanol–sulfuric acid mixture along with how the basicity of the inner-cyclic nitrogen atoms of porphyrin dimer fragments influence the ligand complexation properties towards cations of zinc in ethanol. The increase in the complexation rate when changing the ligands from bis[5-(3-oxyphenyl)-2,8,12,18-

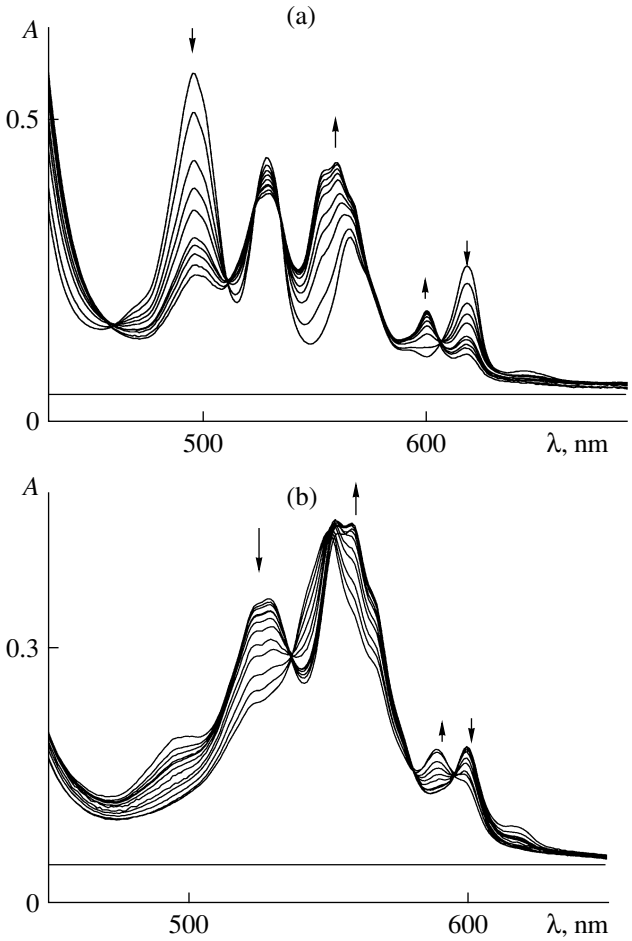


Fig. 2. Changes of EAS of **III** (1.0×10^{-5} mol/l) in the system ethanol-sulfuric acid $c_{H_2SO_4}$ = (0–5×10^{-4}) mol/l (a); (5×10^{-4}–2.5×10^{-3}) mol/l (b).

tetrabutyl-3,7,13,17-tetramethylporphyrinyl]-3,6,9-trioxyundecane-1,11 to bis[5-(3-oxyphenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrinyl]-3,6,9,12-tetraoxytetradecane-1,14 indicates that in the course of complexation, the major contribution to the energy of the transition state comes from the strength of N–H– bonds

Table 3. Complexation rate constants (k_v, l/(mol c)) for porphyrins **III**, **IV**, and **VII** with zinc acetate in ethanol ($c_{porph} = 1.0 \times 10^{-5}$ mol/l $c_{ZnAc_2} = 1.0 \times 10^{-3}$ mol/l), effective rate constants (k_{eff}, s^{-1}), and constants K_{b_1}, and K_{b_2} for processes 1 and 2 in the system C_2H_5OH–H_2SO_4

Porphyrin	$k_{eff} \times 10^4$, s^{-1}		k_v, l mol^{-1} c^{-1} (298 K)	K_{b_1}	K_{b_2}
	298 K	288 K			
III	0.152	0.776	0.280	598	117
IV	96.14	43.26	1.777	573	109
VII*				380	50

* The data is given for 3,7,13,17-tetramethyl-2,8,12,18-tetrabuthylporphyrin (**VII**) from [6].

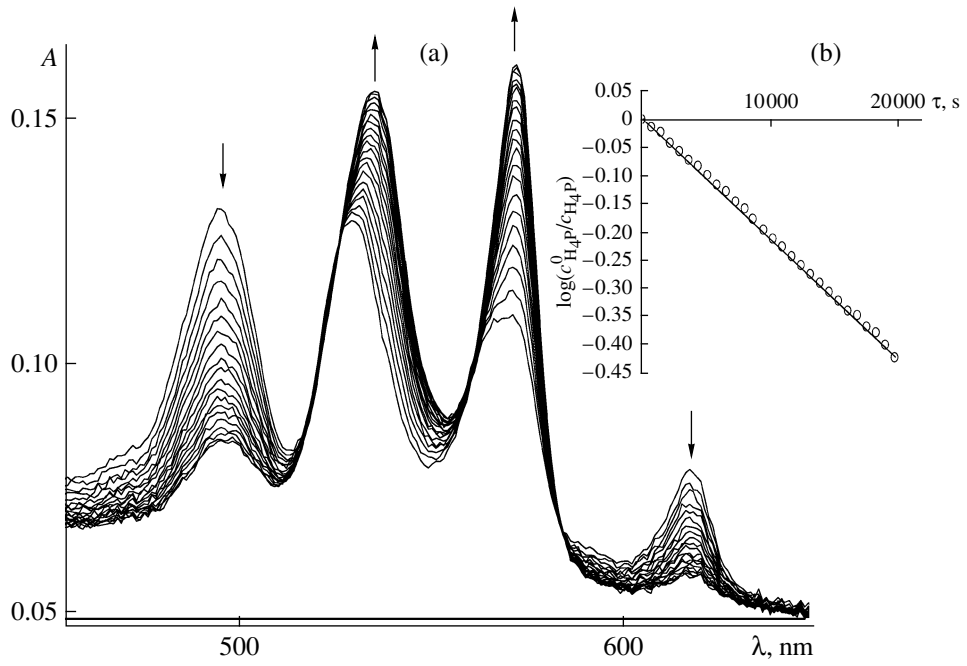


Fig. 3. Changes in absorbance spectra in the course of the complexation reaction between **III** and zinc acetate (a) and $\log(c^0_{H_4P}/c_{H_4P}) = f(\tau)$ for the reaction of zinc bisporphyrinate **I** formation at 298 K in ethanol at $c_{H_4P} = 1 \times 10^{-5}$ mol/l, $c_{ZnAc_2} = 1 \times 10^{-3}$ mol/l (b).

in the porphyrin ligand. Porphyrin with a lower basicity (a higher mobility of N–H) forms the complex with cations of Zn^{2+} six times more rapidly.

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