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Spectrophotometric Study of Acid-Base and Complexing Properties of 5,10,15-Trinitro-2,3,7,8,12,13,17,18-octaethylporphyrin in Acetonitrile

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Abstract—Acid-base and complexing properties of 5,10,15-trinitro-2,3,7,8,12,13,17,18-octaethylporphyrin have been studied by means of spectrophotometry in the acetonitrile/1,8-diazabicyclo[5.4.0]undec-7-ene, acetonitrile/perchloric acid, and acetonitrile/zinc acetate media. The ionization constants and concentration ranges of ionized forms existence have been determined, spectral parameters of the studied porphyrin and its zinc complex have been elucidated, and kinetic parameters of the zinc complex formation have been analyzed.

Keywords: porphyrin, metal complex, kinetics, deprotonation

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Tetrapyrrole compounds are important components of various biological systems providing for numerous vital functions of living organisms [1–3]. Depending on the external conditions such compounds can act as acids or bases, or undergo redox transformations [3, 4]. Available reference data show that in living organisms tetrapyrrole molecules act in the charged (anionic or cationic) form [5, 6]. Such species cannot be easily isolated from the reaction medium. Stable ionic forms of tetrapyrrole molecules can be prepared in vitro via electron detachment from neutral molecule or introduction of excessive electron into the porphyrin macrocycle. Study of the behavior of the so prepared cations and anions allows elucidation of compounds reactivity, intermediates structure, and mechanism of various biochemical, photochemical, complex formation, and other reactions.

The introduction of various substituents (electron donors, electron acceptors, hydrophilic or lipophilic groups) at the porphyrin ring is an efficient means to alter spectral, coordination, catalytic, and other properties of the tetrapyrrole molecules.

Taking into account the recently reported structural data on porphyrins acting in enzyme systems, model studies of the effect of porphyrin macrocycle deformation on spectral, acid-base, and coordination properties of the molecule are of topical importance. In this work we used spectrophotometric titration [7, 8] to investigate acid-base and complexing properties of 5,10,15-trinitro-2,3,7,8,12,13,17,18-octaethylporphyrin (**I**) in the acetonitrile/1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) (**A**), acetonitrile/$HClO_4$ (**B**), and acetonitrile/$Zn(OAc)_2$ (**C**) media (Scheme 1).

Deprotonation and protonation of transannular nitrogen atoms of compound **I** are in general two-stage processes, Eqs. (1)–(4).

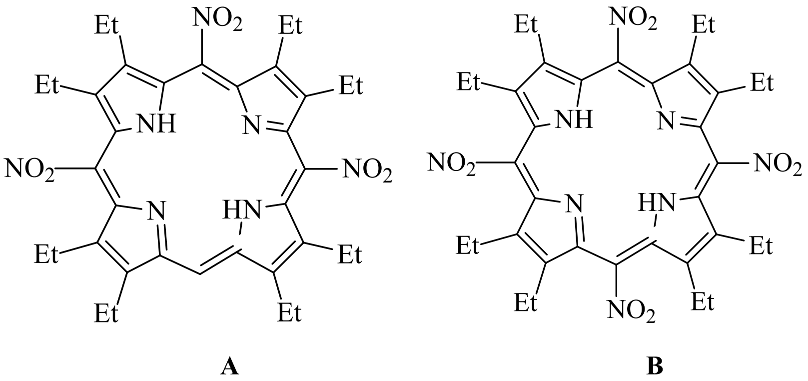
$$H_2P \overset{k_{a1}}{\rightleftarrows} HP^- + H^+, \quad (1)$$

$$HP^- \overset{k_{a2}}{\rightleftarrows} P^{2-} + H^+, \quad (2)$$

$$H_2P + H^+ \overset{k_{b1}}{\rightleftarrows} H_3P^+, \quad (3)$$

$$H_3P^+ + H^+ \overset{k_{b2}}{\rightleftarrows} H_4P^{2+}. \quad (4)$$

Scheme 1.



Hereinafter, H_2P stands for porphyrin **I**; HP^- and P^{2-} are deprotonated forms of compound **I**; H_3P^+ and H_4P^{2+} are protonated forms of compound **I**.

We determined the concentration ranges of ionized forms existence of compound **I** and the corresponding ionization constants. With increasing concentration of the titrant (DBU) in system A from 0 to 1.22 × 10^{-4} mol/L the electron absorption spectrum of neutral form of compound **I** [H_2P, λ_{max}, nm (log ε): 382 (4.54), 510 (3.74), 541 (3.63), 584 (3.53)] was smoothly transformed into that of the dianion [P^{2-}, λ_{max}, nm (logε): 376 (4.31), 502 (4.07)] (Fig. 1a). The spectrophotometric titration curve (λ 382 nm) was step-like, and the presence of two isosbestic points indicated the two-stage deprotonation, Eqs. (1) and (2). The combined constant of the first and the second stages of acid ionization was calculated according to Eq. (5).

$$\log k_A = \log Ind + 2\log c_{DBU}. \qquad (5)$$

In Eq. (5), k_A stands for the combined acid ionization constant to be calculated; *Ind* is the indicator ratio, $[P^{2-}]/[H_2P]$; c_{DBU} is the analytical concentration of DBU in the solution, mol/L.

With increasing concentration of the titrant ($HClO_4$) in system B from 0 to 1.5 × 10^{-4} mol/L the electron absorption spectrum of neutral form of compound **I** was smoothly transformed into that of the dication [H_4P^{2+}, λ_{max}, nm (log ε): 447 (4.64), 593 (3.78), 648(3.69)] (Fig. 1b). The spectrophotometric

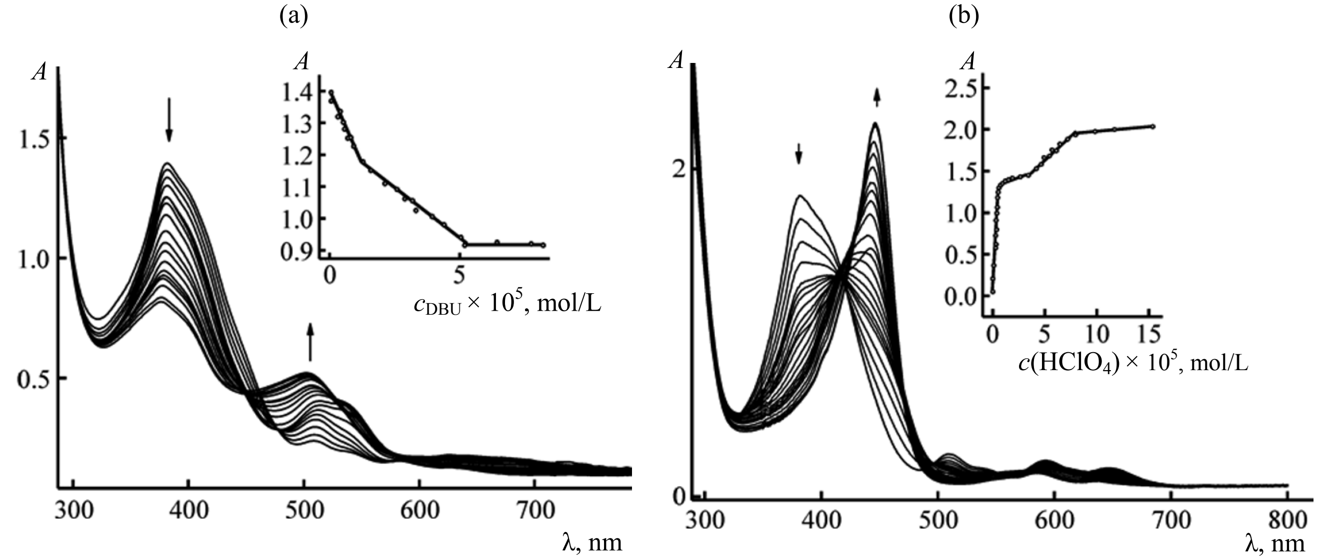


Fig. 1. Evolution of electron absorption spectra and the corresponding titration curves in the course of titration of the porphyrin **I** with DBU (a) and with $HClO_4$ (b) in acetonitrile media at 298 K. c_{DBU} = 0 to 8.22 × 10^{-5} mol/L and c_I = 4.02 × 10^{-5} mol/L (a); $c(HClO_4)$ = 0 to 1.5 × 10^{-4} mol/L and c_I = 5.30 × 10^{-5} mol/L (b).

titration curve (λ 382 nm) was step-like, and the presence of two isosbestic points showed the two-staged protonation, Eqs. (3) and (4). The combined constant of the first and the second stages of base ionization was calculated according to Eq. (6).

$$\log k_B = \log Ind - 2\log c(HClO_4). \quad (6)$$

In Eq. (6), k_B stands for the combined base ionization constant to be calculated; *Ind* is the indicator ratio, $[H_4P^{2+}]/[H_2P]$; $c(HClO_4)$ is the analytical concentration of $HClO_4$ in the solution, mol/L.

The calculated values of the combined acidity and basicity constants of compound **I** at 298 K are collected in the table below along with the corresponding data on the previously studied 5,10,15,20-tetranitro-2,3,7,8,12,13,17,18-octaethylporphyrin **II** and 2,3,7,8,-12,13,17,18-octaethylporphyrin **III** [9] (the constants determination error was ±3–5%).

$\log k$	**I**	**II**	**III**
$\log k_A$	–10.90	–10.44	–
$\log k_B$	10.23	9.56	11.85

Comparison of the determined acidity and basicity constants of compounds **I**–**III** showed that in acetonitrile medium the acid-base properties of the studied porphyrins were dependent on the number of nitro groups in the molecule, due to combination of steric and electronic effects of the substituents [9]. In particular, increasing the nitro groups number in the porphyrin led to the growth of the combined protonation constant in the **III** > **I** > **II** series and to decrease of the combined deprotonation constant in the same series (spectrophotometric titration of compound **III** with the organic base did not detect the presence of any anionic species).

The complexing properties of structurally different β-substituted tetraphenylporphyrins in pyridine or acetic acid medium are known to be dependent on the number of bromine substituents: with more bromine substituents the complex formation constant increases [13]. This unusual effect of the substituents on the properties on the tetraphenylporphyrin has been explained by change of the macrocycle electronic structure due to its spatial distortion and polarization of the N–H bonds.

In order to elucidate the nitro substituents effect on complexing properties of octaethylporphyrinsporphyrins, we investigated kinetics of formation of zinc complex with **I** in system **C** at 298–318 K (Fig. 2). In all cases clear isosbestic points were observed in the spectral series. Parameters of electron absorption spectra of the studied zinc complex coincided with the reference data [10, 11].

The formation of zinc complex of porphyrin **I** can be expressed by Eq. (7).

$$H_2P + [ZnX_2(Solv)_{n-2}] \rightarrow ZnP + 2HX + (n-2)Solv, \quad (7)$$

where X, acidic ligand; Solv, solvent molecule; *n*, zinc ion coordination number.

The reaction kinetic parameters were calculated following the well known method, expressed by Eqs. (8)–(11). First, the effective reaction rate constant k_{eff} was determined following Eq. (8):

$$\begin{aligned} k_{eff} &= (1/t)\ln [c^0(H_2P)/c(H_2P)] \\ &= (1/t)\ln [(A_0 - A_\infty)/(A - A_\infty)], \end{aligned} \quad (8)$$

with *t*, time passed from the reaction start; A_0, A_t, and A_∞ absorption of the reaction mixture: initial, at time *t*, and final, correspondingly. The true reaction rate on the $(n + 1)$ order k_{n+1} was calculated using Eq. (9).

$$k_{n+1} = k_{eff}/c^n_{salt}, \quad (9)$$

where c_{salt}, zinc acetate concentration.

The activation energy was calculated from the reaction rate constants determined at different temperatures using integrated form of the Arrhenius equation (10); the activation entropy was calculated using Eq. (11) from the rate constant at 298 K.

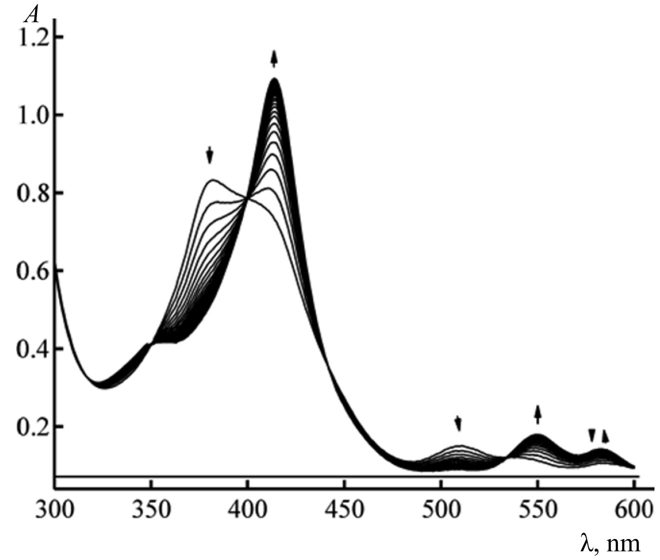


Fig. 2. Kinetic series of electron absorption spectra in the course of coordination of the porphyrin **I** with zinc acetate in acetonitrile medium at 298 K.

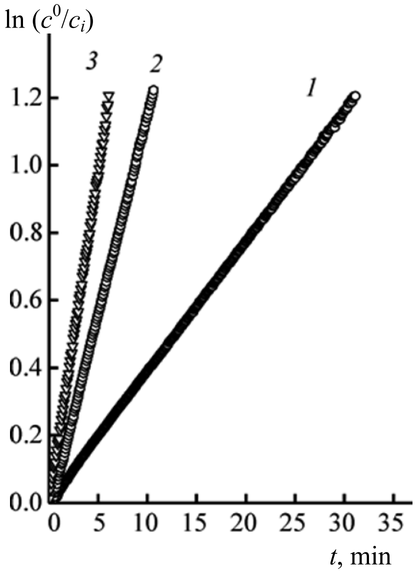


Fig. 3. Kinetics of ln (c_0/c_i) change in the course of formation of zinc complex with the porphyrin **I** in acetonitrile medium: determination of the reaction order with respect to porphyrin. (*1*) 298 K; (*2*) 308 K; (*3*) 318 K; $c_{\mathbf{I}} = 2.32 \times 10^{-5}$ mol/L; $c[Zn(OAc)_2] = 2.35 \times 10^{-3}$ mol/L.

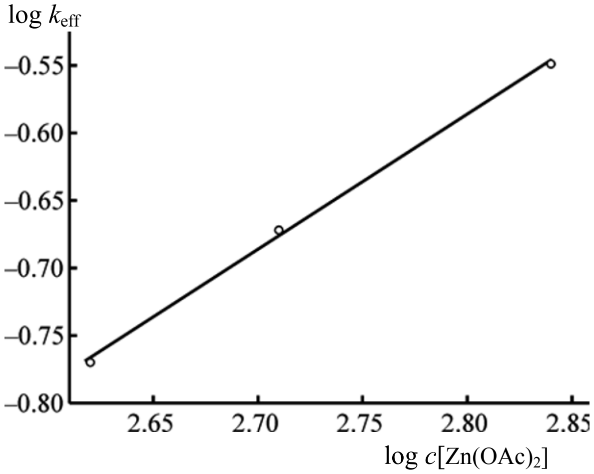


Fig. 4. Determination of the reaction rate order, with respect to zinc acetate, of formation of zinc complex with the porphyrin **I**, at 298 K in acetonitrile medium (slope 0.999, the correlation coefficient 0.9998).

$$E_a = R[T_1T_2/(T_2 - T_1)]\ln(k_2/k_1), \quad (10)$$

$$S^{\neq} = R[\ln(k_{298}/298) + E_a/(298R) - \ln(k_B/h)], \quad (11)$$

where k_B, Boltzmann constant; R, gas constant; h, Planck's constant.

At each temperature, the measurements were run at least in triplicate. The reaction rate order with respect to porphyrin was determined by analysis of the log $[c^0(H_2P)/c(H_2P)]$ plots versus time (Fig. 3). The reaction rate order with respect to zinc acetate was determined from the slope of the log k_{eff} versus log $c[Zn(OAc)_2]$ plot (Fig. 4). Kinetic parameters of the formation of zinc complexes with porphyrins **I–III** are given in the table below [9]. It could be anticipated that introduction of strong electron-acceptor nitro groups should weaken the N–H bond at the reactive site, and therefore accelerate the reaction (7). The collected experimental data show that with more of nitro groups in the porphyrin macrocycle, the reaction (7) was indeed accelerated. The energy of the zinc complex formation was approximately equal in the cases of all the studied porphyrins; however, the activation entropy of the complex formation decreased in the **III** < **I** < **II** series. Likely, the nitro-containing derivatives of octaethylporphyrin are kind of dissipative structures, leading to alternation of the system equilibrium due to structural rearrangement of porphyrin molecule. The spatially distorted *meso*-substituted octaalkylporphyrins reveal stronger acid properties as compared with the unsubstituted analog. The deformation of the macrocycle resulting from introduction of the nitro groups decreases likely the molecule aromaticity and isolates π-electron systems of the pyrrole and pyrrolenine fragments, thus enhancing acidity of compounds **I** and **II** and accelerating the complex formation reaction.

Kinetic parameters of coordination reaction (7) of porphyrins **I**–**III** with zinc acetate in acetonitrile medium

Comp. no.	$[Zn(OAc)_2]$, mol/L	k^{298}, L mol s^{-1}	ΔE, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
I	2.35×10^{-3}	73±2	50±4	–3±1
II	2.35×10^{-3}	81±3	54±5	12±1
III	2.56×10^{-3}	64±2	47±4	–15±1

EXPERIMENTAL

Electron absorption spectra were recorded using Shimadzu UV1800, Hitachi U2000 Cary 100 Varian spectrophotometers.

5,10,15-Trinitro-2,3,7,8,12,13,17,18-octaethylporphyrin was prepared as described elsewhere [10, 11].

Details of spectrophotometric experiments and the data processing are to be found in [7, 8].

Zinc acetate (analytically pure grade) was purified by recrystallization from aqueous acetic acid and dehydrated at 380–390 K [12].

REFERENCES

1. Alonso, C.M.A., Neves, M.G.P.M.S., Tomé, A.C., Silva, A.M.S., Cavaleiro, J.A.S., *Tetrahedron Lett*., 1997, vol. 38, no. 15, p. 2757.
2. Vicente, M., Jaquinod, L., Khoury, R., Mandrona, A., and Smith, K.M., *Tetrahedron Lett*., 1999, vol. 40, no. 50, p. 8763.
3. Novak, B.H. and Lash, T.D., *J. Org. Chem*., 1998, vol. 63, no. 12, p. 3998.
4. *The Rorphyrin Handbook*, Kadish, K.M., Smith, K.M., and Guilard, R., Eds., San Diego: Academic, 2000, vol. 6, p. 280.
5. Kiselev, Yu.M., *Khimiya koordinatsionnykh soedinenii* (Chemistry of Coordinated Compounds), Moscow: Integral-Press, 2008.
6. Shul'ga, A.M., Sinyakov, G.N., and Gurinovich, G.P., *Biofiz.*, 1978, vol. 23, no. 1, p. 5.
7. Ivanova, Yu.B., Churakhina, Yu.I., and Mamardashvili, N.Zh., *Russ. J. Gen. Chem*., 2008, vol. 78, no. 4, p. 673. DOI: 10.1134/S1070363208040269.
8. Ivanova, Yu.B., Sheinin, V.B., and Mamardashvili, N.Zh., *Russ. J. Gen. Chem*., 2007, vol. 77, no. 8, p. 1458. DOI: 10.1134/S1070363207080270.
9. Ivanova, Yu.B., Chizhova, N.V., Pukhovskaya, S.G., and Mamardashvili, N.Zh., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 5, p. 939.
10. Watanabe, E., Nichimura, S., Ogoshi, H., and Yoshida, Z., *Tetrahedron*, 1975, vol. 31, no. 11, p. 1385.
11. Gong, L.-S. and Dolphin, D., *Canad. J. Chem*., 1985, vol. 63, no. 2, p. 401.
12. Karyakin, Yu.V. and Angelov, I.I., *Chistye khimicheskie reaktivy* (Pure Chemical Reactives), Moscow: Khimiya, 1974.