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# Spectrophotometric Study of Equilibrium Association of Cationic Acids of Tetraphenylporphyrin β-Bromo-Derivatives in Acetonitrile–Perchloric Acid System at 298 K

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**Abstract**—The basic properties of 2-bromo-5,10,15,20-tetraphenylporphyrin (**I**), 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin (**II**) and 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin (**III**) in the system of acetonitrile–perchloric acid at 298 K were studied using a method of spectrophotometric titration. The protonation of endocyclic nitrogen atoms of tetrapyrrole macrocycles was found to occur in two stages, therewith the increase in the number of bromine atoms in the structure of the macrocycle made easier the addition of the first proton compared with the second one. The ionization constant and the concentration ranges of existence of mono- and dication forms of the compounds were determined.

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The porphyrin-containing systems that are used as the molecular mechanisms become a common phenomenon of the modern chemistry [1–6]. Porphyrins and structurally related phthalocyanines are the obejcts of thorough investigation for their possible use in LCD monitors and light-absorbing materials. Further investigation of porphyrin analogs is stimulated by the ability of their modified chromophore systems to absorb in the red and infrared regions of the spectrum while maintaining the properties associated with the porphyrin core [2, 3]. At the moment, along with the traditional syntheses to increase the porphyrin macrocycle of great interest are the syntheses with the formation of substituents in the pyrrole rings. These compounds were used as molecular probes and photosensors in cancer therapy (thiadiazoloporphyrins), and as geochemical standards in the analysis of metalloporphyrins in sediments [7]. In order to further explore these tetrapyrrole compounds, we performed this work aimed at the spectrophotometric study of unusual tetraphenylporphyrin β-bromo-derivatives, in which the bromine atoms were in the pyrrole rings of the macrocycle.

We have studied the basic properties of 2-bromo-5,10,15,20-tetraphenylporphyrin (**I**), 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin (**II**) and 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin (**III**) in the system acetonitrile–perchloric acid [Eq. (1)] at the standard temperature by the method of spectrophotometric titration [8].

The process of protonation of the nitrogen atoms of the tetrapyrrole macrocycles **I–III** occurs at the endocyclic nitrogen atoms in two steps, [Eqs. (1) and (2)]:

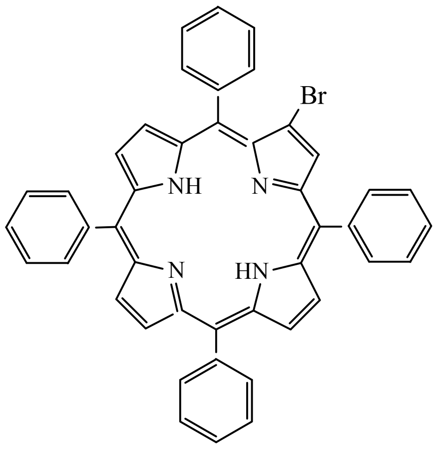
$$H_2P + H^+ \overset{k_{b1}}{\rightleftarrows} H_3P^+, \qquad (1)$$

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

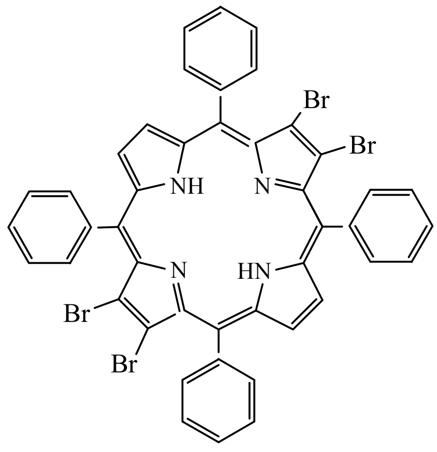
Here $H_3P^+$ and $H_4P^{2+}$ are first and second protonated forms, respectively, of compounds **I–III.**

We established the concentration ranges of existence of mono- and dication forms of porphyrins **I–III** and the corresponding ionization constants.

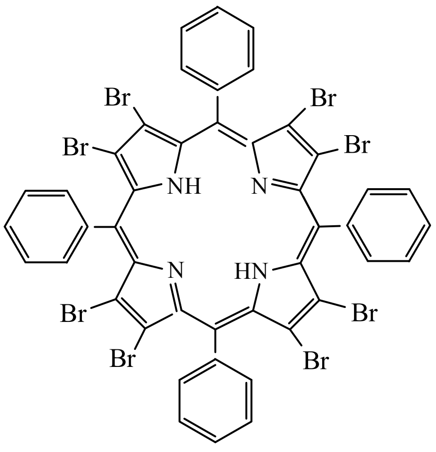
At the titration of compound **I** in the system (1) ($c_{porph}$ = 3.91×10$^{-4}$ M) with increasing concentration of perchloric acid ($c$(HClO$_4$) = 0–4.19×10$^{-5}$ M) in the electron absorption spectrum a formation was observed of two sets of spectral curves, and to each set



**I**



**II**



**III**

corresponded its own set of isobestic points and its own step in the titration curve (Figs. 1–5). The electron absorption spectrum of the molecular form ($H_2P$) of compound **I** corresponded to the following parameters: λ 415 (log ε 4.22), λ 516 (log ε 3.14), λ 594 (log ε 2.82), and λ 647 (log ε 2.85). With increasing concentration of titrant [$c(HClO_4) = 0–1.4\times10^{-5}$ M] the electronic spectrum gradually transformed into that of the monoprotonated form ($H_3P^+$): λ 451 (log ε 4.12), λ 676 (log ε 3.43), and at [$c(H_2SO_4)= 1.4\times10^{-5}–4.19\times 10^{-5}$ M], into the final shape of dication ($H_4P^{2+}$) with the parameters of the spectrum: λ 446 (log ε 4.25), λ 671 (log ε 3.37). By determining the coordinates of the inflection point (and the corresponding concentration of perchloric acid) on the titration curve (Fig. 1) we distinguished two areas in the electron absorption spectrum of the reaction system that correspond to the first and second stages of ionization, that is, to the formation of mono- and diprotonated forms (1, 2) of compound **I**. According to Eq. (3) we calculated consistently the protonation constants of the first and second steps for both the processes. The values of the basicity constants in acetonitrile–perchloric acid at 298K for the compound **I** are listed below.

$$\log k_b = \log(\text{Ind}) - n\log c_{ac}, \qquad (3)$$

| Constants | I | II | III |
|---|---|---|---|
| $\log k_1$ | 5.39 | 5.47 | 6.71 |
| $\log k_2$ | 5.02 | 4.78 | 4.06 |

where $k_b$ is the basicity constants for the first or second step; Ind is the indicator ratio $H_3P^+/H_2P$ for the first

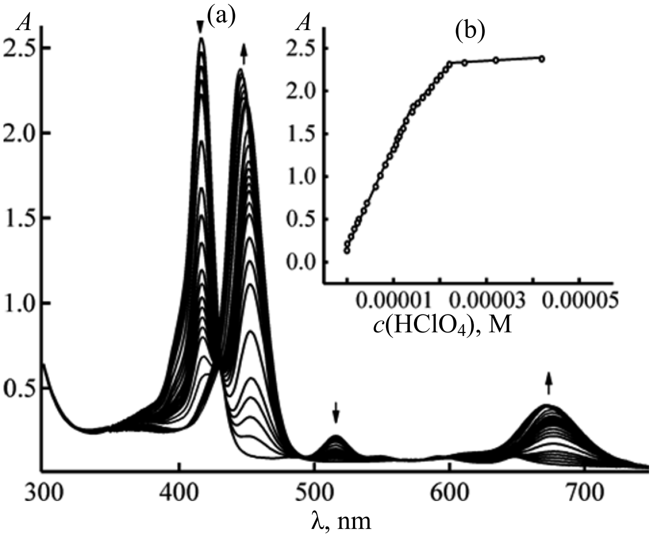


**Fig. 1.** (a) Changes in the EAS and (b) spectrophotometric titration curve of compound **I** ($c_{porph} = 3.91\times10^{-4}$ M) in the system of $HClO_4–CH_3CN$ ($0–2.5\times10^{-5}$ M) at 298 K.

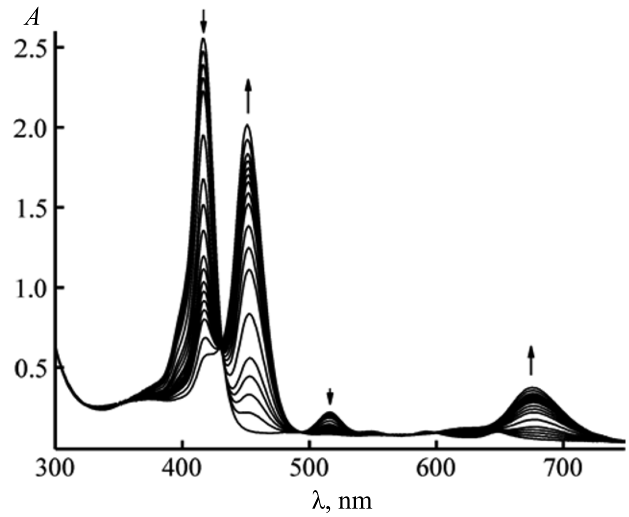


**Fig. 2.** Changes in the EAS of compound **I** ($c_{porph}$ = $3.91\times10^{-4}$ M) in the system of $HClO_4–CH_3CN$ ($0–1.4\times 10^{-5}$ M) at 298 K.

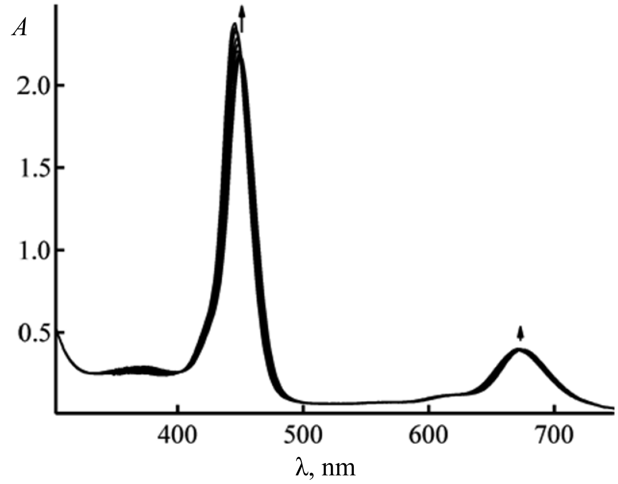


**Fig. 3.** Changes in the EAS of compound **I** ($c_{\text{porph}}$ = 3.91×10$^{-4}$ M) in the system of $HClO_4$–$CH_3CN$ (0–1.4×10$^{-5}$–2.5×10$^{-5}$ M) at 298 K.

step and $H_4P^{2+}/H_3P^+$ for the second step; $c_{\text{ac}}$ is the analytical concentration of perchloric acid in solution.

Increase in the number of bromine atoms in the tetraphenylporphin macrocycle to four corresponds to compound **II**. At the titration of compound **II** ($c_{\text{porph}}$ = 9.97×10$^{-5}$) in the system (1) at standard temperature the electron absorption spectrum of the molecular form ($H_2P$) containing the peaks λ 431 (log ε 4.20), λ 537 (log ε 3.25), λ 693 (log ε 3.15 ) was converted into the spectrum of the monoprotonated form ($H_3P^+$): λ 467 (log ε 4.22), λ 705 (log ε 3.53) [$c$($HClO_4$) = 0–9.74×10$^{-6}$ M] and then into the electronic spectrum of the diprotonated form ($H_4P^{2+}$): λ 465 (log ε 4.36), λ 699 (log ε 3.63) [$c$($H_2SO_4$) = 9.74×10$^{-6}$–1.69×10$^{-4}$ M] (Fig. 4)a. The titration curve (Fig. 4b) corresponds to two stages, each of which is in line with a set of spectral curves with the isosbestic point in the electron spectrum. The coordinates of the inflection point were determined and the ionization constants were calculated as in the case of compound **I**. The protonation constants of compound **II** are listed above.

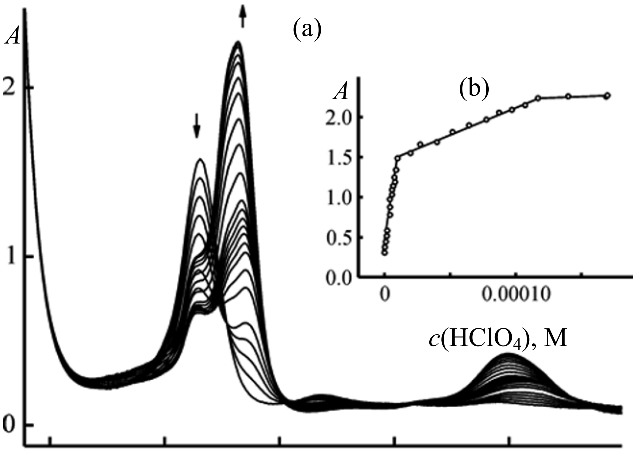


**Fig. 4.** (**a**) Changes in the EAS and (b) spectrophotometric titration curve of compound **II** ($c_{\text{porph}}$ = 9.97×10$^{-5}$ M) in the system of $HClO_4$–$CH_3CN$ (0–2.5×10$^{-5}$ M) at 298 K (analytical wavelength 464 nm).

Further increase in the number of bromine atoms to eight in the macrocycle corresponds to structure **III**. At the titration of compound **III** ($c_{\text{porph}}$ = 3.22×10$^{-5}$ M) in the system (1) at standard temperature the EAS of the molecular form ($H_2P$) [λ 470 (log ε 4.16), λ 636 (log ε 3.56)] transformed into that of monoprotonated form ($H_3P^+$): λ 490 (log ε 4.32), λ 732 (log ε 3.72) [$c$($HClO_4$) = 0–2.18×10$^{-7}$ M] and then in the electronic spectrum of the diprotonated form ($H_4P^{2+}$): λ 489 (log ε 4.56), λ 742 (log ε 3.89) [$c$($H_2SO_4$) = 2.18×10$^{-7}$–5.38×10$^{-4}$ M] (Fig. 5a). The titration curve (Fig. 5b) reflects two stages, each of which corresponds to the set of their spectral curves with the isosbestic point. The procedure for determining the point of inflection on the titration curve and calculation of ionization constants were the same as in the case of compounds **I** and **II**. The values of the constants are listed above.

The data obtained indicate that the complication of the molecule associated with an increase in the number of bromine atoms in the macrocycle affects ambiguously the reactivity of the bromo-substituted β-tetraphenylporphyrins: The increase occurs in the basic properties of the first stage of protonation and the

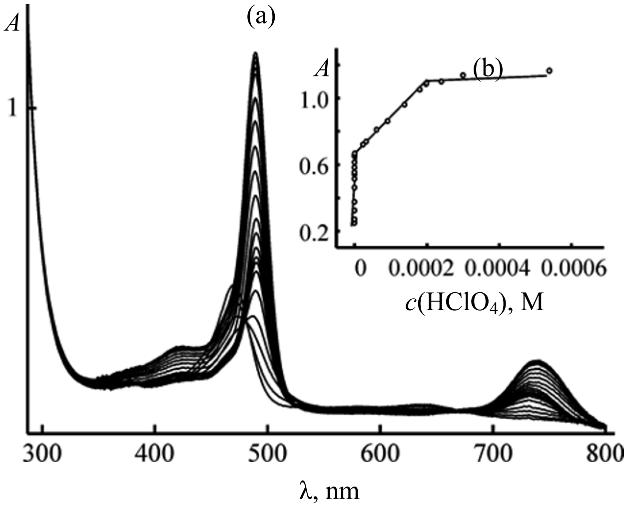


**Fig. 5.** (**a**) Changes in the EAS and (b) spectrophotometric titration curve of compound **III** ($c_{\text{porph}}$ = 3.22×10$^{-5}$ M) in the system of $HClO_4$–$CH_3CN$ (0–3×10$^{-4}$ M) at 298 K.

decrease in the second stage of protonation. Values of log $k_1$ of the first stage increase in the series **III > II > I**, while the values of log $k_2$ are reduced in the series **III < II < I**. These experimental facts are well known in the literature and are reflected in the complexing properties of similar tetrapyrrole macrocycles [13, 14]. In particular, it is known that the reaction rate of complex formation by the β-substituted tetraphenylporphyrins of diverse structures in pyridine and acetic acid vary depending on the number of bromine atoms and the nature of the solvent: The additional introduction of bromine in the structure of tetraphenylporphine increases the rate constant of the complex formation [15,16]. This unusual effect of the bromine atoms on the basic properties of the bromine-substituted β-tetraphenylporphins probably are associated with the changes in electronic structure of the macrocycle of the molecule due to the spatial distortion of the molecule and as a consequence of the polarization of NH bonds.

## EXPERIMENTAL

Porphyrins **I–III** were obtained by the methods described in [8–10]. The spectrophotometric titration with perchloric acid in acetonitrile was performed on a Varian Cary 100 spectrophotometer. The experimental procedure, preparative chemistry, and the experimental data were presented in detail in [11,12]. The error in determining the corresponding constants was ±3–5%.

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