ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 3, pp. 545–549. © Pleiades Publishing, Ltd., 2014.
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Basicity of Octa- and Dodecamethyl-substituted Tetraphenylporphyrins by Phase-Transfer Spectral Potentiometric Titration

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Received December 19, 2013

Abstract—Phase-transfer potentiometric titration with potentiometric pH control in the system chloroform–aqueous electrolyte solution was used to determine basicity constants for octamethyl-substituted tetraphenylporphyrins. The pH ranges were determined, where the dicationic form of octa- and dodecamethyl-substituted tetraphenylporphyrins is prevailing. It was shown that the basicity of tetraphenylporphyrins is increased by methyl substitution of β-hydrogens (formation of octamethyl-substituted tetraphenylporphyrins). Further methylation of the four central nitrogen atoms of the porphyrin (formation of dodecamethyl-substituted tetraphenylporphyrins) extends the dication stability pH range to 12.

DOI: 10.1134/S1070363214030220

Porphyrins are amphotheric compounds, i.e. can behave both as acids and as bases [1]. Porphyrins can add one or two protons by the imine nitrogens to form a mono- (H_3P^+) or a dicatiom (H_4P^{2+}), or to donate two pyrrole protons to form a mono- (HP^-) or a dianion (P^{2-}).

The interest in protonated porphyrins is associated with the fact that they hold promise as membrane-active components of anion-selective electrodes and can also serve as useful models for correlating steric and acid–base properties of porphyrins [2–6].

In the present work we focused exclusively on the basic equilibria of octamethylporphyrins in phase-transfer system comprising a chloroform porphyrin solution and an aqueous electrolyte solution [Eqs. (1), (2)].

$$H_4P^{2+} \leftrightarrow H_3P^+ + H^+, K_4, \quad (1)$$

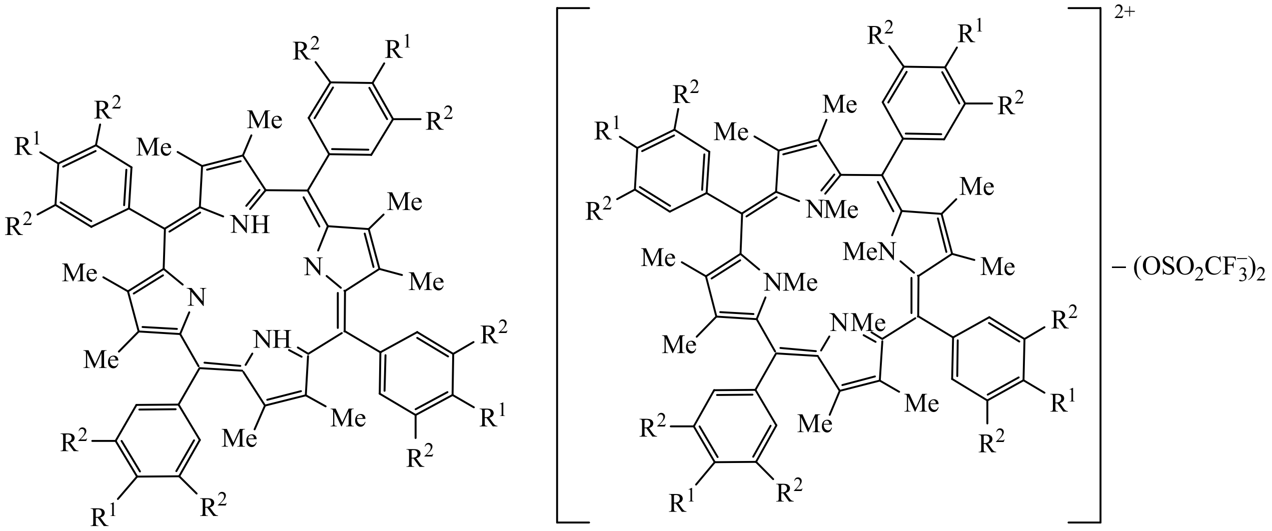
$$H_3P^+ \leftrightarrow H_2P + H^+, K_3. \quad (2)$$

At present porphyrin complexes are fairly successfully used in membranes of anion-selective electrodes. However, the electrochemical characteristics of porphyrin membranes are pH-sensitive. In the case of tetraphenylporphyrins, anions can be selectively detected only in the pH range, where the porphyrin exists in the dicationic form. Therefore, it is important to consider tetraphenylporphyrins methylated by the central nitrogen atoms, which exist as dications.

Octamethyl-substituted porphyrins, i.e. porphyrins methylated by the periphery of the porphyring ring, have scarcely been studied, whereas dodecamethylporphyrins, i.e. porphyrins methylated both by the periphery and by the central nitrogen atoms have long been considered as hardly synthesizable. Senge et al. [7] showed that porphyrins can be methylated by their inner nitrogen by small C-electrophiles, and such porphyrins exist as dications. Methyl trifluoromethanesulfonate is a suitable reagent for such synthesis.

The objects for study were the following octamethyl-substituted tetraphenylporphyrins: 2,3,7,8,12,-13,17,18-octamethyl-5,10,15,20-tetraphenylporphyrin (**I**), 5,10,15,20-tetrakis(4-*tert*-butylphenyl)-2,3,7,8,12,-13,17,18-octamethylporphyrin (**II**), and 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-2,3,7,8,12,13,17,18-octamethylporphyrin (**III**), as well as structurally related dodecamethyl-substituted tetraphenylporphyrins: 2,3,7,8,12,13,17,18,21,22,23,24-dodecamethyl-5,10,15,20-tetraphenylporphyrin bis(trifluoromethylsulfonate) (**IV**), 5,10,15,20-tetrakis(4-*tert*-butylphenyl)-2,3,7,8,12,13,17,-18,21,22,23,24-dodecamethylporphyrin bis(trifluoromethylsulfonate) (**V**), and 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-2,3,7,8,12,13,17,18,21,22,23,24-

Scheme 1.



I–III **IV–VI**

$R^1 = R^2 = H$ (**I, IV**); $R^1 = C(CH_3)_3$ $R^2 = H$ (**II, V**); $R^1 = H$, $R^2 = C(CH_3)_3$ (**III, VI**).

dodecamethylporphyrin bis(trifluoromethylsulfonate) (**VI**) (Scheme 1).

By phase-transfer spectropotentiometric titration we determined ranges, where the porphyrins exist as dications, and studied dependence of their spectral characteristics on the pH of the aqueous electrolyte solution contacting the chloroform porphyrin solution.

The electronic absorption spectra (EAS) allow one to judge about the state of the π-electron system of the porphyrin molecule. From changes in the positions and intensities of absorption bands we can correlate molecular structures and spectral properties of porphyrins [8].

The EAS of octamethyl-substituted tetraphenylporphyrins **I**, **II**, and **III** are similar to each other. Figure 1 shows the EAS of porphyrin **II** at varied pH of aqueous $NaClO_4$ solutions.

Under conditions of equilibrium with aqueous solutions of acids, the EAS of octamethyl-substituted tetraphenylporphyrins in chloroform look like the spectrum of porphyrin in the dicationic form H_4P^{2+} [9]. As the pH of aqueous solutions contacting chroloform

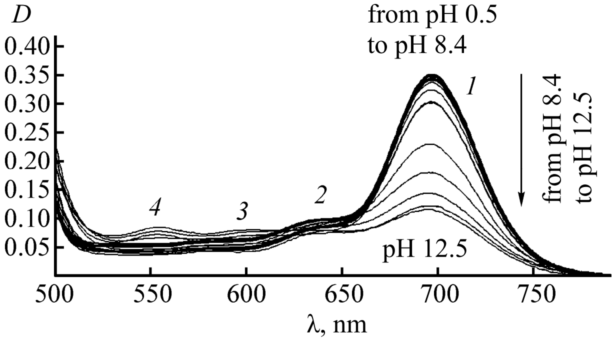


Fig. 1. Electronic absorption spectra of 5,10,15,20-tetrakis-(4-*tert*-butylphenyl)-2,3,7,8,12,13,17,18-octamethylporphyrin (**II**) on pH of their contacting aqueous $NaClO_4$ solutions. For (*1*–*4*) see text.

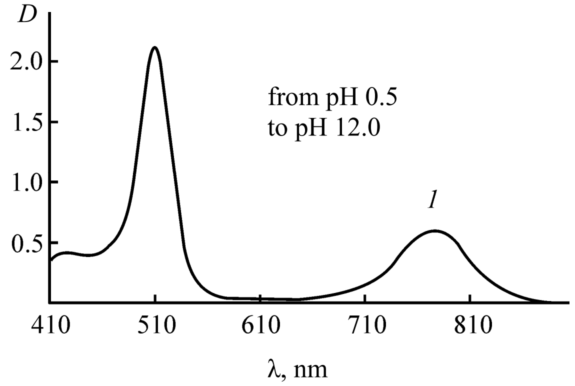


Fig. 2. Electronic absorption spectra 5,10,15,20-tetrakis(4-*tert*-butylphenyl)-2,3,7,8,12,13,17,18,21,22,23,24-dodecamethylporphyrin bis(trifluoromethylsulfonate) (**V**) are not dependent on the pH of aqueous $NaClO_4$ solutions. For (*1*) see text.

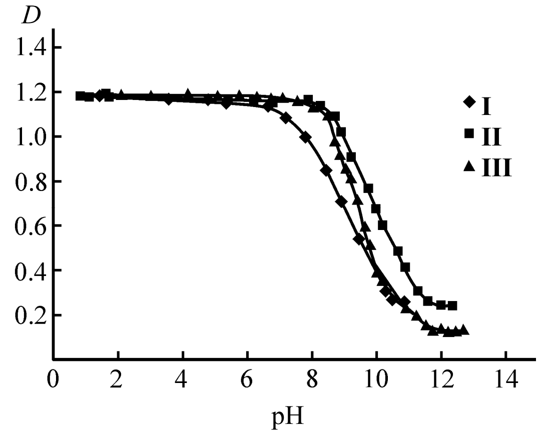


Fig. 3. Dependence of the optical density (*D*) of octamethyltetraphenylporphyrin solutions on the pH of their contacting aqueous $NaClO_4$ solutions.

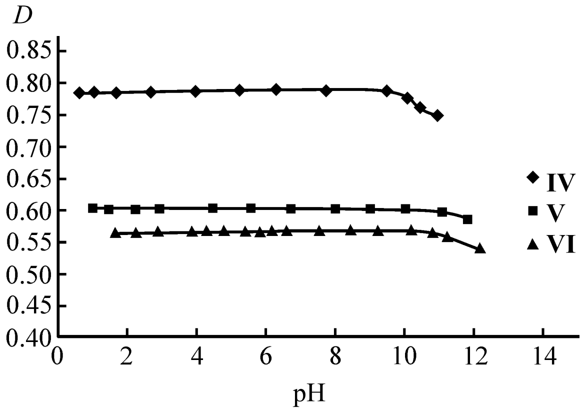


Fig. 4. Dependence of the optical density (*D*) of dodecamethyltetraphenylporphyrin solutions on the pH of their contacting aqueous $NaClO_4$ solutions.

solutions of octamethyltetraphenylporphyrins is increased, the intensity of absorption band *1* does not change until pH 8.4. On further increase of pH, band *1* sharply decreases in intensity and shifts blue. Simultaneously, bands *3* and *4* (characteristics of the neutral form of the porphyrin) appear and grow, implying occurrence of deprotonation reactions (1) and (2). The EAS in the visible range show no isosbestic point, providing evidence for the presence of the monocation H_3P^+. Consequently, we can calculate separately the basicity constants K_3 and K_4.

The EAS of dodecamethyl-substituted tetraphenylporphyrins **IV**, **V**, and **VI**, too, are similar to each other. Figure 2 shows the EAS of compound **V**. As seen, the optical density is independent of the pH of aqueous $NaClO_4$ solutions over the entire experimental pH range (0.5–12.0).

Under conditions of equilibrium with aqueous solutions of acids, the EAS of dodecamethyl-substituted tetraphenylporphyrins in chloroform look like the spectrum of porphyrin in the dicationic form H_4P^{2+} [9]. As the pH of aqueous solutions contacting chroloform solutions of dodecamethyltetraphenylporphyrins is increased, the shape and intensity of bands in the EAS remain absolutely invariable until pH 12. Consequently, such porphyrins are stable dications over a wide pH range.

When the two phases are in equilibrium, ion exchange takes place between the $OSO_2CF_3^-$ and ClO_4^-, which explains the invariable spectral characteristics of the porphyrin.

We obtained plots of the optical densities (*D*) of the porphyrin solutions against the pH of aqueous $NaClO_4$ solutions, contacting with them (Figs. 3 and 4). The plots were constructed using the *D* values for band *1*. The pHs of aqueous solutions contacting the organic phase were measured with a glass electrode.

$HClO_4$, (NaOH)

AgCl | AgCl, KCl_{sat} | NH_4NO_{3sat} | $NaClO_4$(1 M.) | glass electode |

(aqueous phase)

$\uparrow\downarrow$

Porphyrin solution

(organic phase)

The plots for octamethyl-substituted tetraphenylporphyrins have a stepwise shape and characteristically show a sharp decline of optical density at pH > 8.4. With dodecamethyl-substituted tetraphenylporphyrines, we observe that the optical density is complexly independent of pH over a wide pH range. The pH

Table 1. pH Ranges of existence of porphyrins **I–VI** in the dicationic form

Comp. no.	R = Ph	pH
I	H	<6.7
II	4C(CH$_3$)$_3$	<8.4
III	3,5-C(CH$_3$)$_3$	<8.4
IV	H	<9.7
V	C(CH$_3$)$_3$	<12.0
VI	3,5-C(CH$_3$)$_3$	<12.0

ranges, where porphyrins **I–VI** are present in the dicationic form, are shown in Table 1.

Mathematical processing of the spectra obtained by phase-transfer titration [10] allowed us to calculate the basicity constants pK_3 and pK_4 of octamethyl-substituted tetraphenylporphyrins **I–III**. The calculation was based on the maximum of band *1* in the EAS of the porphyrins, reactions (3) and (4), and Eqs. (5) and (6).

$$\mathrm{H_2P^{org} + HClO_4^{aq} \leftrightarrow [H_3P]^{+}ClO_4^{-org}}, K_3, \tag{3}$$

$$\mathrm{[H_3P]^{+}ClO_4^{-org} + HClO_4^{aq} \leftrightarrow [H_4P]^{2+}(ClO_4^{-})_2^{org}}, K_4, \tag{4}$$

$$\mathrm{p}K_3 = \mathrm{pH} - \log a_{\mathrm{ClO_4^-}} \log (D_\mathrm{m} - D_\mathrm{x})/(D_\mathrm{x} - D_1)], \tag{5}$$

$$\mathrm{p}K_4 = \mathrm{pH} - \log a_{\mathrm{ClO_4^-}} \log [(D_\mathrm{o} - D_\mathrm{x})/(D_\mathrm{x} - D_\mathrm{m})]. \tag{6}$$

Here D_o is the optical density of porphyrin in the dicationic form; D_m, optical density of porphyrin in the monocationic form; D_x, optical density of mixed forms; and D_l, optical density of the neutral form.

The basicity constants pK_3 and pK_4 depend on the acid-base properties of the porphyrin and on the nature of the anion and organic solvent. The basicity constants of octamethyl-substituted tetraphenylporphyrins are listed in Table 2.

We showed in the present work that the basicity of porphyrins can be increased not only by donor substitution over the periphery of the phenyl fragment of the porphyrin ring, but also by substitution of peripheral β-hydrogen atoms, for instance, by methyl groups (to form octamethyl-substituted tetraphenylporphyrins).

Dodecamethyl-substituted porphyrins can be recommended as membrane-active components for anion-selective electrodes capable of operating in a wide pH range.

Table 2. Experimental basicity constants of octamethyl-substituted tetraphenylporphyrins

Comp. no.	Substituent	pK_3, ±0.1	pK_4, ±0.1
IV	H	8.0	9.7
V	4C(CH$_3$)$_3$	8.7	10.4
VI	3,5-C(CH$_3$)$_3$	8.8	10.2

EXPERIMENTAL

Octa- and dodecamethyl-substituted tetraphenylporphyrins were synthesized at the Ivanovo State University of Chemical Technology. The absorption maxima of the porphyrins in chloroform solutions were as follows, λ_max, nm: 552 (Soret), 687 (**I**); 471 (Soret), 690 (**II**); 473 (Soret), 697 (**III**); 506 (Soret), 759 (**IV**); 510 (Soret), 778 (**V**); 513 (Soret), 777 (**VI**).

Detailed description the method of phase-transfer spectral potentiometric titration and rationalization of its use for studying acid–base equilibria in porphyrins are given in [10–12].

The organic solvent used in the present work phase-transfer spectral potentiometric titration was chloroform which was chosen because it is immiscible with water and provides sufficient solubility of the ionic forms of the studied porphyrins.

The experimental temperature was 22 ± 1°C. The electrochemical cell contained porphyrin dissolved in chloroform, as well as 1 M NaClO$_4$ as background electrolyte. Titration was initiated at pH 0.5. The pHs of aqueous solutions were measured with an I-130 ionometer with an ESL-41G-07 glass electrode calibrated by standard buffer solutions. Titration was performed with NaOH with a pH step of ~ 0.3. The criterion of established phase equilibrium was a constant EMF of the galvanic element. After complete separation of the aqueous and organic phases, a sample of the organic phase was taken for spectral measurements on a Shimadzu UV-1650 instrument.

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