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pH-Switchable Porphyrin Receptor for Binding Halide Ions

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Abstract—Main properties of 5,10,15,20-tetra(4-chlorophenyl)porphyrin in the acetonitrile–perchloric acid system were studied by the method of spectrophotometric titration at standard temperature. The protonation of nitrogen atoms of the tetrapyrrole macrocycle was shown to occur in two steps, through the formation of mono- and diprotonated forms. The corresponding ionization constants and concentration intervals were determined. The diprotonated form of porphyrin was shown to bind effectively iodide, bromide and chloride ions, the stability constants of the complexes of 1:1 and 1:2 composition were determined.

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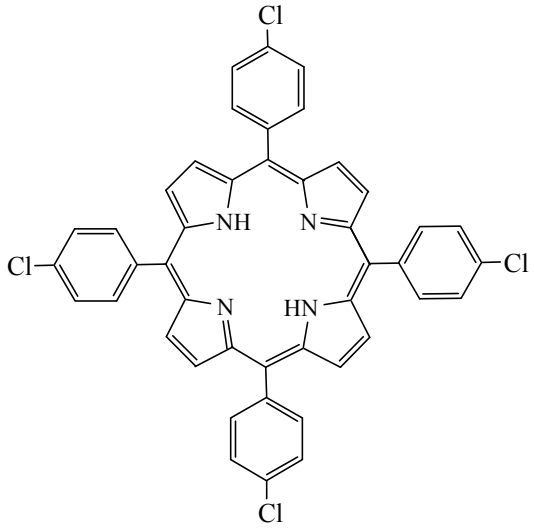
The building up of effective receptors for detection of chemical and biological compounds is a topical problem of the modern science [1]. The protonated forms of tetrapyrrole macrocycles, being excellent chromophores, bind selectively anions by their conformationally labile complexing cavity [2–5]. Pronounced electron donor or electron acceptor properties of the created receptors are defined largely by the acidity function of the medium. The use of relatively simple methods of spectral analysis to determine anions in solution makes these studies extremely popular. Due to the increasing interest in the development of selective tetrapyrrole receptors for anions, in this study we carried out a direct titration of the 5,10,15,20-tetra(4-chlorophenyl)porphyrin (H_2P, **I**) diprotonated (H_4P^{2+}) forms with solutions of $(C_4H_9)_4NI$, $(C_4H_9)_4NBr$, and $(C_2H_5)_4NCl$. We found that the H_4P^{2+} effectively binds halide anions in acetonitrile at 298 K. The stability constants of the formed complexes of 1:1 and 1:2 composition and the concentration ranges of their existence were determined.

The porphyrin (H_2P) molecules in acid acetonitrile media [2,6] are protonated at the tertiary nitrogen atoms with the formation of mono- (H_3P^+) and dications (H_4P^{2+}) [Eqs. (1), (2)]. We studied by the spectrophotometric titration method the basic properties of compound **I**. The titration was carried out in acetonitrile medium with perchloric acid of the concentration of 0.01 M. The perchloric acid solution was prepared in acetonitrile. In these circumstances perchloric acid is fully dissociated and the protonation occurs with a solvated proton [7].



5,10,15,20-Tetra(4-chlorophenyl)porphyrin (**I**).

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

$$H_3P^+ + H^+ \underset{}{\overset{k_{b2}}{\rightleftharpoons}} H_4P^{2+}, \quad (2)$$

$$H_2P–CH_3CN–HClO_4. \quad (3)$$

Upon the titration of the tetrapyrrole macrocycle with perchloric acid (Fig. 1) the electron absorption spectra (EAS) indicate successive formation of the

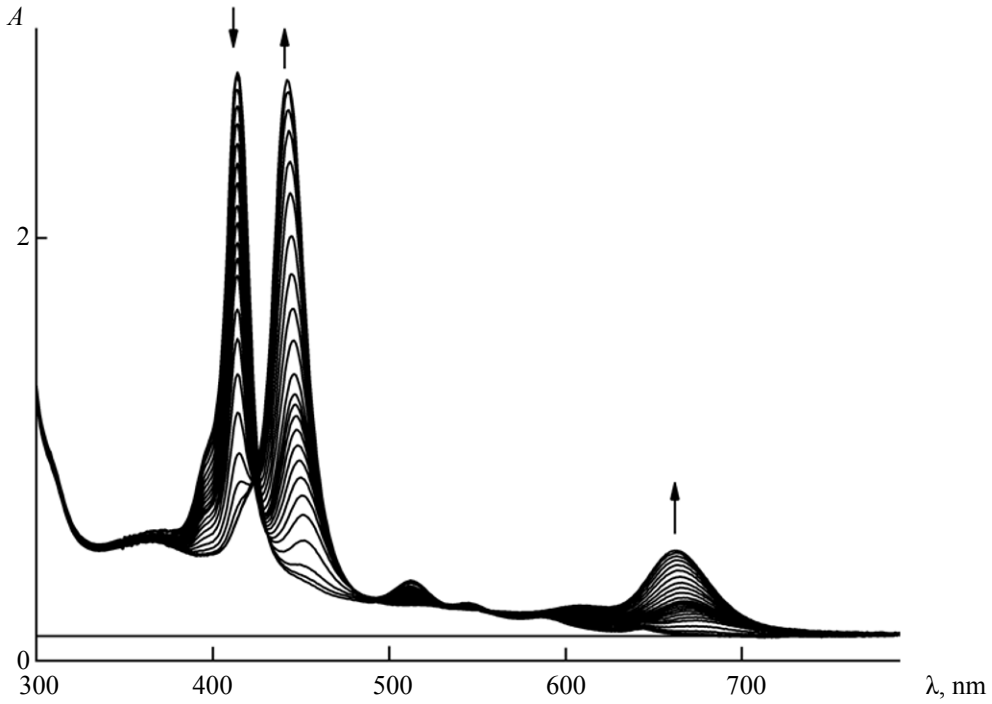


Fig. 1. Spectrophotometric titration of **I** ($C_{porph.}$ = 3.5×10^{-5} M) in the system of acetonitrile–perchloric acid in the region of $HClO_4$ concentrations from 0 to 1×10^{-4} M.

H_3P^+ and H_4P^{2+} forms. At the increase in the concentration of perchloric acid the peaks of the five-band absorption spectrum of the molecular form of **I** suffer a red shift with the gradual transformation of the spectrum first into a four-band (H_3P^+), and then in two-band (H_4P^{2+}) spectrum (Fig. 1). The parameters of EAS of compound **I** in the system (3) for various forms of the ligand are given in Table 1.

The corresponding titration curve (Fig. 2) includes two steps, to each one corresponds its family of spectral curves in the EAS. Determining the coordinates of the inflection point in the titration curve as described in [6], we separated the protonation processes in the system (3) into the steps, and calculated the corresponding constants for the processes (1), (2) according to formula (4).

Table 1. Parameters of electron absorption spectra of some forms of compound **I** (C_{porph} ~2×10^{-5} M) and their complexes with halide ions in acetonitrile in the presence of $HClO_4$ (0 to 10^{-3} M)

Form	λ_1, nm (log ε)	λ_2, nm (log ε)	λ_3, nm (log ε)	λ_4, nm (log ε)	λ_5, nm (log ε)
H_2P	413 (5.26)	512 (4.41)	546 (4.31)	587 (4.27)	644 (4.21)
H_3P^+	414 (5.24)	446 (5.03)	512 (4.31)	–	668 (4.20)
H_4P^{2+}	439 (5.24)	–	–	–	660 (4.41)
H_4PI^+	442 (4.20)	–	–	–	671 (3.57)
H_4PI_2	444 (4.11)	–	–	–	680 (3.55)
H_4PBr^+	445 (5.14)	–	–	–	660 (4.39)
H_4PBr_2	451 (5.09)	–	–	–	671 (4.37)
H_4PCl^+	443 (5.18)	–	–	–	666 (4.38)
H_4PCl_2	448 (5.16)	–	–	–	668 (4.36)

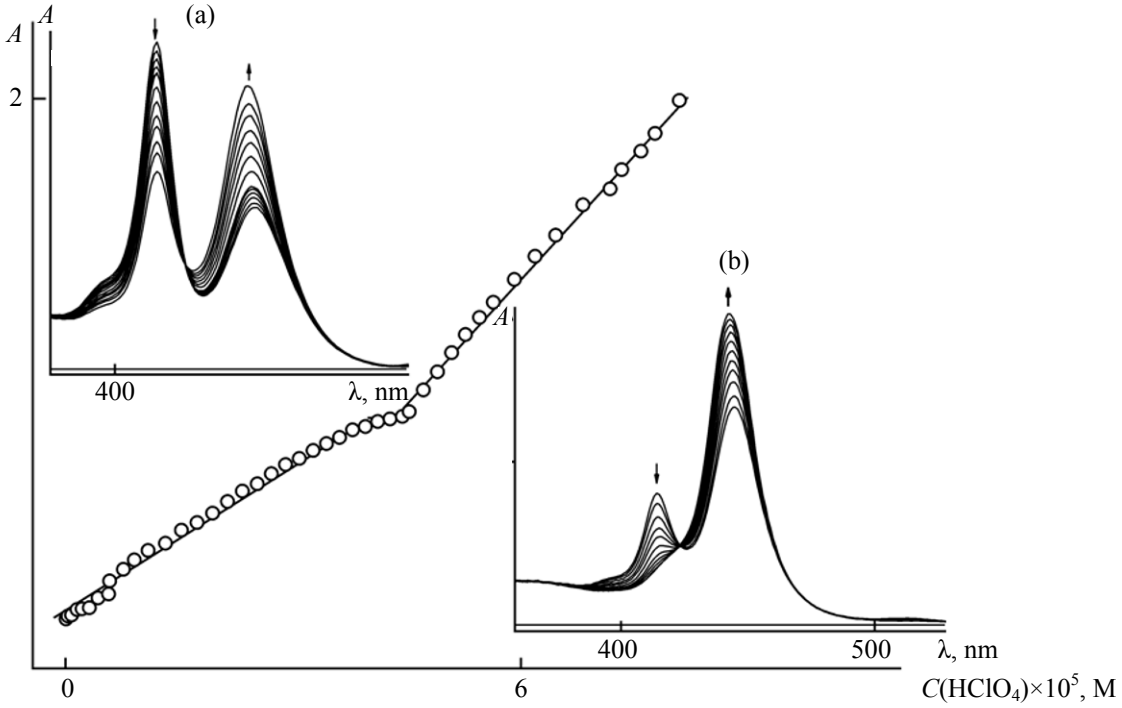


Fig. 2. Spectrophotometric titration of **I** in acetonitrile by perchloric acid at the analytical wavelength λ = 445 nm; C_{porph} = 3.5×10^{-5} M, the region of $HClO_4$ concentrations from 0 to 1×10^{-4} M: (a) the step of the formation of H_3P^+, (b) 2nd step, the formation of H_4P^{2+}.

$$\log k_b = \log (Ind) - n\log c_{ac}, \quad (4)$$

where k_b is the basicity constant for the respective first or second step, Ind is the indicator ratio H_3P^+/H_2P for the first step and H_4P^{2+}/H_3P^+ for the second step; c_{ac} is the analytical value of the perchloric acid concentration in the solution, M, n = 1 (the number of added protons formed at the dissociation of perchloric acid).

At each point the values of the reagent analytical concentrations was corrected for dilution of the working solution according to Eq. (5).

$$A_т = A^0_т/(1 + \Sigma_\Delta V/V_0), \quad (5)$$

where V_0 is the initial volume of the solution, $\Sigma_\Delta V$ is the total value of the added titrant, and A_T is the current value of the optical density at the analytical wavelength with accounting for the added titrant, A^0_T is the current value of the optical density at the analytical wavelength.

The values of the protonation constants of the first and second stages are 1.6×10^5 and 2.1×10^4 M^{-1}, respectively. The error in the determination of the constants was calculated as the arithmetic mean value of the constants obtained in three parallel experiments, and amounted to 5–7%.

The results of spectrophotometric titration showed that system (3) passes three areas of concentration of perchloric acid, where **I** exists as H_2P (≤3×10^{-7} M), H_3P^+ (4.1×10^{-5} to 4.4×10^{-5} M) and H_4P^{2+} (≥7.5×10^{-5} M). The data obtained allowed us the performance of a direct titration of the dication **I** solutions with $(C_4H_9)_4NI$, $(C_4H_9)_4NBr$ and $(C_2H_5)_4NCl$ in the systems (6)–(8) at 298 K for the investigation of a possibility to use the protonated porphyrins as receptors for halide ions X^-.

$$H_2P–HClO_4–(C_4H_9)_4NI–CH_3CN, \quad (6)$$

$$H_2P–HClO_4–(C_4H_9)_4NBr–CH_3CN, \quad (7)$$

$$H_2P–HClO_4–(C_2H_5)_4NCl–CH_3CN. \quad (8)$$

The results of titration of H_4P^{2+} with the iodide ion [system (6)] are shown as the ESP pattern (Fig. 3) and the titration curve (Fig. 4). Upon increase in the iodide ion [I^-] concentration, in the EAS of the H_4P^{2+} solution a sequential formation occurs of two series of spectral curves (each series has its isobestic point), which probably belong to the equilibria (9), (10).

$$H_4P^{2+} + I^- \overset{k_1}{\rightleftharpoons} (H_4P^+)I, \quad (9)$$

$$(H_4P^+)I + I^- \overset{k_2}{\rightleftharpoons} H_4PI_2. \quad (10)$$

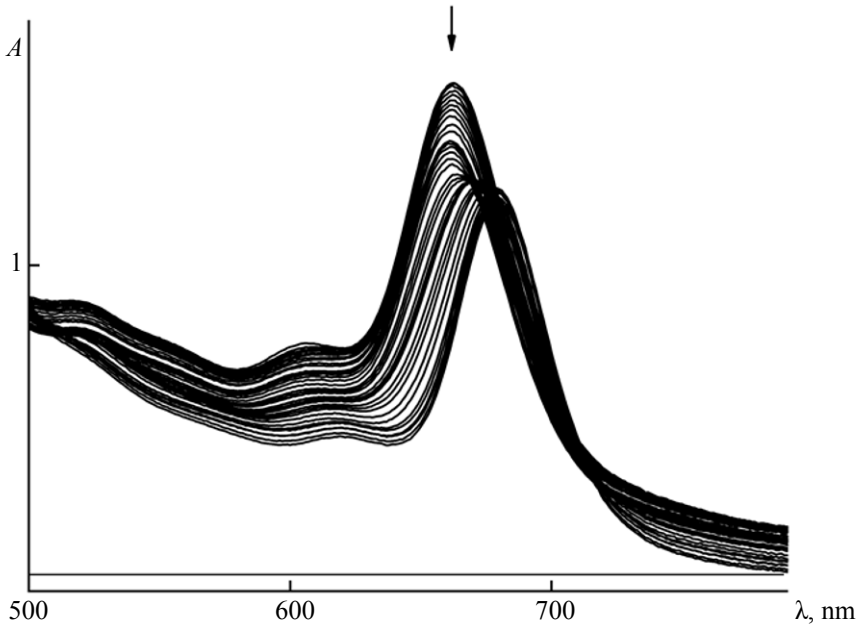


Fig. 3. Changes in the electron absorption spectra of the system H_4P^{2+} ($C = 5.5\times10^{-5}$ M) – $(C_4H_9)_4NI$ ($C = 0–1.2\times10^{-3}$ M) – $HClO_4$ ($C = 9.9\times10^{-5}$ M) – CH_3CN.

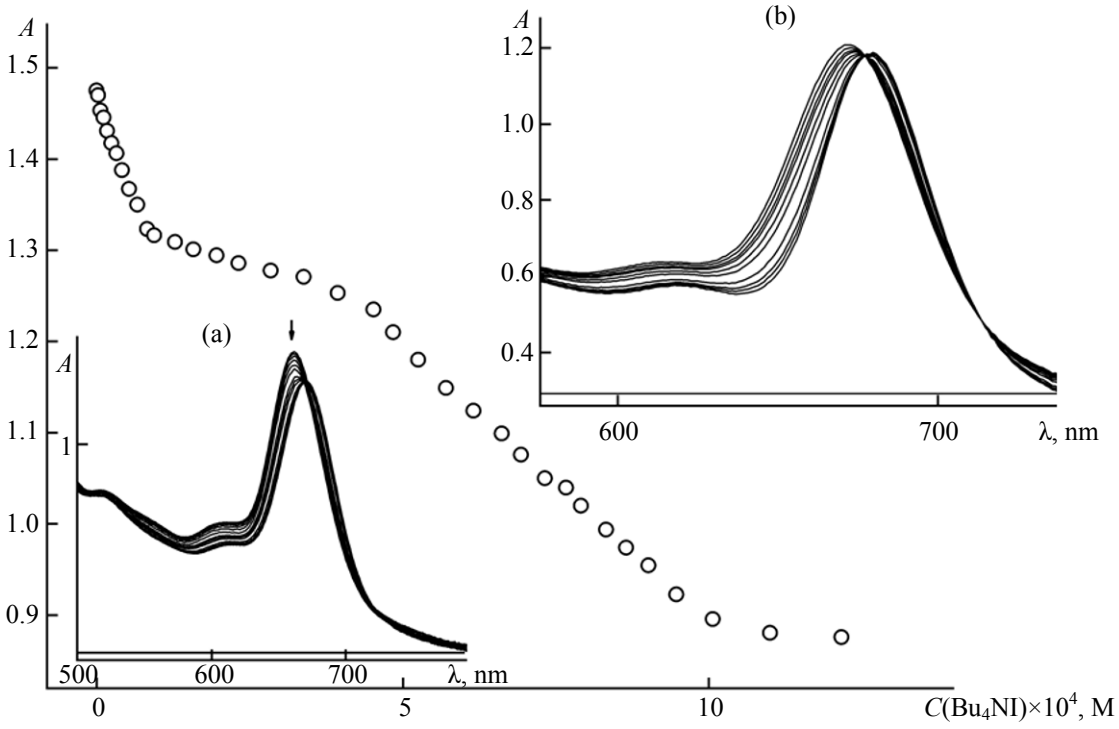


Fig. 4. Titration curve of the **I** dication in the system (6) at the analytical wavelength λ = 662 nm: (a) step 1, formation of H_4PI^+; (b) step 2, formation of H_4PI_2.

A possibility of the existence of the porphyrin associates of this kind was established [8] by X-ray analysis.

In the electron absorption spectrum the maximal red shift (~20 nm) of the absorption band with the maximum at the analytical wavelength λ = 662 nm is observed (Fig. 3)

It has been published that alkilammonum halide salts dissociate in the acid–acetonitrile solutions and as by-product of associates form the associates of the type H_nX_m [4, 9–11], where X is halide. Effect of the H_nX_m associates in the process of binding the halide anions by tetrapyrrole macrocycle halide cations to form AH in the range pH = 3–18 was studied potentiometrically using a glass electrode, reference silver chloride electrode, and the ion-selective electrodes for halide ions (Cl^-, Br^-, I^-) in a standard spectropotentiometric cell [4, 10, 11].

The straight-line relationship pI = *f*(pH) (Fig. 5) shows that at the concentration of perchloric acid 7.5×10^{-5} M (experimental conditions) among the byproducts in the system (6) there are no associates of the H_nX_m type with iodine. Taking this into account we calculated the formation constants of H_4PI^+ and H_4PI_2 for the equilibria (9), (10) by Eq. (11).

$$\log k = \log (\text{Ind}) - n\log c_x, \qquad (11)$$

where k is the association constant of the first or second steps (7), (8), respectively; Ind is Indicator ratio $(H_4P^+X)/H_4P^{2+}$ for the first stage, and $(H_4PH_2)/(H_4P^+X)$ for the second; c_x is the analytical concentration of the halide salt in solution in M, n = 1 (the number of the added halide ions). The error in the determination of the constants has been calculated as the arithmetic mean value of the constants obtained in three parallel experiments, it amounted to 5–7%. The values of the constants are listed in Table 2.

The results of titration of H_4P^{2+} with the bromide ions [system (7)] are seen from the EAS and the titration curve (Fig. 6). Upon increase in the concentration of bromide [Br^-], in the EAS of the H_4P^{2+} solutions occurs a sequential formation of two series of spectral curves. Each series has its own isosbestic point [the processes (12) and (13)].

$$H_4P^{2+} + Br^- \underset{}{\overset{k_1}{\rightleftharpoons}} (H_4P^+)Br, \qquad (12)$$

$$(H_4P^+)Br + Br^- \underset{k_2}{\rightleftharpoons} H_4PBr_2. \qquad (13)$$

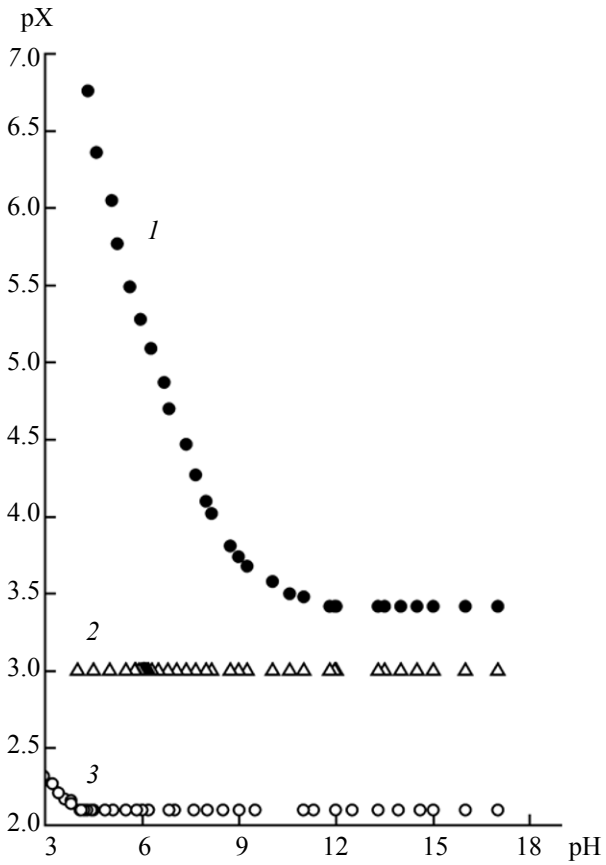


Fig. 5. Dependences of pX = *f*(pH) in acetonitrile at 298 K, X = (*1*) Cl, (*2*) I, and (*3*) Br[16].

During the entire titration a gradual red shift (11 nm) of the absorption bands was observed. The intensity of the bands decreased, and the extinction coefficients (Table 1) gradually diminished. After determining the coordinates of the inflection points on the titration curve the association processes in the system (7) were separated into steps and by formula (11) the corresponding constants for the processes (12), (13) were calculated. At the concentration of perchloric acid 7.5×10^{-5} M (experimental conditions) among the byproducts of the system (7) the hydrobromic as-

Table 2. Association constants of the complexes $(H_4P^+)X^-$ and H_4RX_2 in CH_3CN

$[X^-]$	k_1	k_2
$[I^-]$	2.45×10^4	1.29×10^3
$[Br^-]$	9.55×10^4	6.92×10^3
$[Cl^-]$	1.38×10^6	1.99×10^5

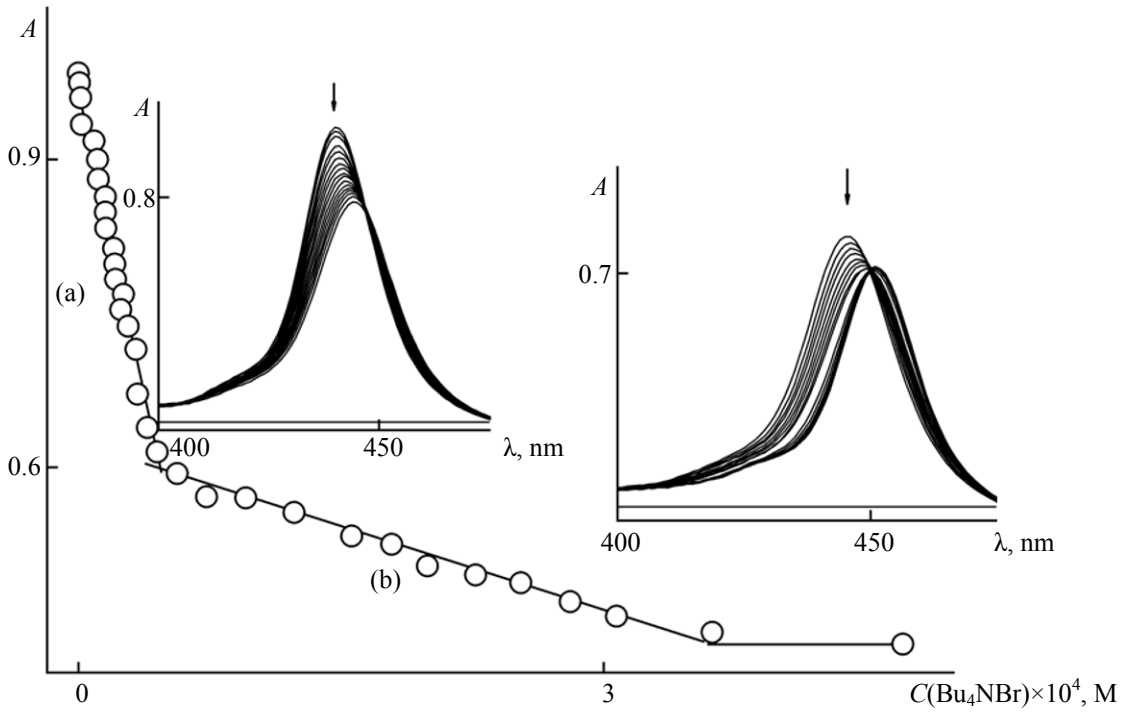


Fig. 6. Changes in the electron absorption spectra of the system (7): H_4P^{2+} (5.6×10^{-6} M)–$(C_4H_9)_4NBr$ (0–3.5×10^{-4} M)–$HClO_4$ (1.1×10^{-5} M) – CH_3CN and the titration curve of the compound **I** dication in the system (7) at the analytical wavelength λ = 440 nm: (a) first step, formation of H_4PBr^+, (b) second step, formation of H_4PBr_2.

sociates were not detected (Fig. 5). The numerical values of the constants of formation of $(H_4P^+)Br$ and H_4PBr_2 are listed in Table 2.

The results of titration of H_4P^{2+} with chloride ions [system (8)] are seen from the data of the EAS and the titration curve (Fig. 7). Upon increase in the concentration of chloride ions [Cl^-], in the EAS of the H_4P^{2+} solutions also the consecutive formation of two series of spectral curves was observed, each series had its isobestic point [processes (14) and (15)].

$$H_4P^{2+} + Cl^- \underset{}{\overset{k_1}{\rightleftharpoons}} (H_4P^+)Cl, \quad (14)$$

$$(H_4P^+)Cl + Cl^- \underset{}{\overset{k_2}{\rightleftharpoons}} H_4PCl_2. \quad (15)$$

In the EAS throughout the titration a gradual red shift of the absorption bands (8–9 nm) was observed. The intensity of the bands decreased and, consequently, the extinction coefficient gradually diminished (Table 1). It should be noted that the red shift was the lowest compared with the values of a similar shift in the spectra of iodide and bromide associates (Table 1).

For system (8) the formation constants (Table 2) of H_4PCl^+ (k_1) and H_4PCl_2 (k_2) [equilibria (14) and (15)] were calculated according to Eq. (9) taking into account the formation of associates of the form H_nCl_m. At the perchloric acid concentration 7.5×10^{-5} M (experimental conditions) among the byproducts of the system (8) were found the associates like HCl, H_2Cl^+, HCl_2^-, HCl_3^{2-} [processes (16)–(19)] with the following values of the association constants: $K(H_2Cl^+)$ (pK = 4.76), K_{HCl} (pK = 8.39), $K(HCl_2^-)$ (pK = 2.65), and $K(HCl_3^{2-})$ (pK = 3.61).

$$H^+ + HCl \rightarrow H_2Cl^+, K(H_2Cl^+), \quad (16)$$

$$H^+ + Cl^- \rightarrow HCl, K_{HCl}, \quad (17)$$

$$HCl + Cl^- \rightarrow HCl_2^-, K(HCl_2^-), \quad (18)$$

$$HCl_2^- + Cl^- \rightarrow HCl_3^{2-}, K(HCl_3^{2-}). \quad (19)$$

From the Eqs. (16)–(19) and the material balance Eq. (20), we can construct Eq. (21), which connects all the current chlorine concentration.

$$C_0 = Cl + HCl + H_2Cl^+ + 2HCl_2^- + 3HCl_3^{2-}, \quad (20)$$

$$C_0 = \{1 + [a]K_{HCl} + [a]^2K_{HCl}K(H_2Cl^+)\}[Cl^-] + 2[a]K_{HCl}K(HCl_2^-)[Cl^-]^2 + 3[a]K_{HCl}K(HCl_2^-)K(HCl_3^{2-})[Cl^-]^3, \quad (21)$$

where C_0 is the analytical concentration of Et_4NCl at each point, [Cl^-] is the current concentration of

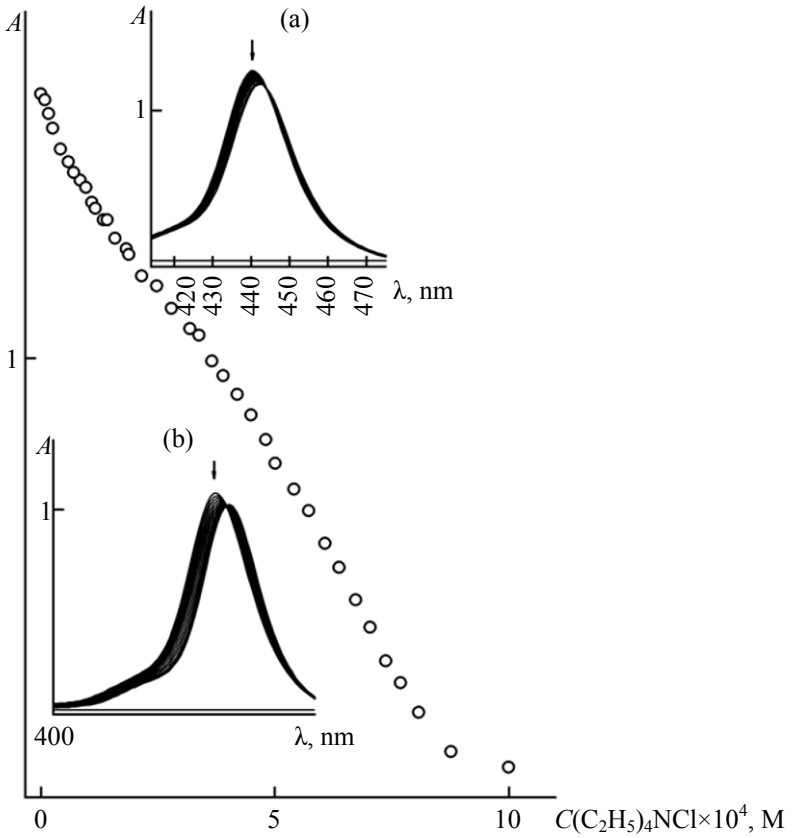


Fig. 7. Changes in the electron absorption spectra at the analytical wavelength λ = 440nm for the system (8): H_4P^{2+} (6×10^{-6} M)–$(C_2H_5)_4NCl$ ($0–8\times10^{-4}$ M)–$HClO_4$ (1.1×10^{-5} M)–CH_3CN and the titration curve of the compound **I** dication in the system (8) on the analytical wavelength λ = 440 nm: (a) the first step, formation of H_4PCl^+, (b) second step, formation of H_4PCl_2.

chlorine, [*a*] is the active concentration of hydrogen ions measured by a glass electrode. Substituting in this equation the values of analytical concentration of Et_4NCl at each point and the value of active concentration of hydrogen ion, we obtain a system of cubic equations like (22).

$$C_0 = p[Cl^-] + [Cl^-]^2[Cl^-]^3. \quad (22)$$

This system can be simply enough solved to obtain the true values of the $[Cl^-]$ concentration in the solution.

Table 1 contains the parameters of the EAS in a series of $I^-–Br^-–Cl^-$ for the transitions of $(H_4P^+)X$ to H_4PH_2 and H_4P^{2+} to H_4PH_2. In the first case, the band shift values were 7, 5 and 3 nm, in the latter case 20, 11 and 8 nm, respectively. The data in Table 2 show that the association constant of diprotonated forms of compound **I** are maximal in the case of chloride associates and is minimal for iodide associates. The formation of the iodide associates is much more complicated compared with the bromide and chloride associates. One can assume that the iodide anion due to its high volume and low ionic potential cannot approach the coordination center of the dication to a distance sufficient for the formation of hydrogen bonds with hydrogen atoms of the NH groups, whereas for the anions of bromine and chlorine with lower values of ionic radii these processes are more probable. In all three systems the spectral responses of the system to the change in its state can easily be recorded and indentified. The sensitivity of the proposed macroheterocycle (the band shift and change in intensity in the visible region of the absorption spectra) covers a wide concentration range of the measured analyte concentrations (from 10^{-6} to 10^{-3} M), which allows to use the porphyrin chromophores as the basic compounds for the creation of pH-switchable molecular sensors capable of forming an analytical signal due to chemical interaction with the receptor molecules of the substrate.

EXPERIMENTAL

Acetonitrile from Aldrich was not additionally purified. The water content was determined by Fischer method, and it did not exceed 0.04%. Solutions of $(C_4H_9)_4NI$ and perchloric acid were prepared in acetonitrile. The choice of tetraalkylammonium salts was determined by the value of the association constants in acetonitrile [12–15]. All salts were purified in a Soxhlet apparatus with acetonitrile and dried in a vacuum (1.33 Pa) at 393K to constant weight. The method of spectro-photometric titration in acetonitrile was described in detail in [2, 6].

Porphyrin **I** was synthesized by the following procedure. A mixture of pyrrole (0.67 g, 0.01 mol) and 4-chlorbenzaldehyde (1.40 g, 0.01 mol) in propanoic acid (350 ml) was boiled for 30 min. The reaction mixture was cooled, the precipitate was filtered off and successively washed with methanol, hot water, and again methanol. The residue on the filter was dried and chromatographed on aluminum oxide, eluent is a mixture of CH_2Cl_2 and C_6H_{14}, 1:1. Yield 0.97 g, 56%. R_f 0.37 (Al_2O_2, CH_2Cl_2–C_6H_{14}, 1:1). Found,%: C 70.18, H 3.42; N 7.41. $C_{44}H_{26}N_4Cl_4$. Calculated,%: C 70.21, H 3.46; N 7.45. 1H NMR spectrum ($CDCl_3$), δ, ppm: 8.70 s (8H, β-CH of pyrrole), 7.60 d (8H, ArH-*o*), 7.19 d (8H, ArH-*m*), –2.81 s (2H, NH). EAS (acetonitrile), λ_{max}, nm (log ε): 644 (4.21) 587 (4.27), 546 (4.31) 512 (4.41), 413 (5.26).

ACKNOWLEDGMENTS

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