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Electrochemical Properties and Spectrophotometry of Membranes Based on Holmium Tetraphenylporphyrinchloride

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Abstract—Protolytic properties of holmium tetraphenylporphyrinchloride were studied by the method of two-phase spectrophotometric titration with potentiometric monitoring of pH of the medium. Apparent constants of the heterophase reaction of the exchange of an anion for the hydroxide ion were determined. It was found that the membranes based on holmium tetraphenylporphyrinchloride with dibutyl phthalate as a solvent-softener are selective to ions of alkaline earth metals (Ca^{2+} and Ba^{2+}) in the region of pH > 7 over the concentration range from 1 up to 1×10^{-4} M. Selectivity coefficients were determined by two independent methods: the method of biion potentials and the method of mixed solutions. The found selectivity series coincides with traditional Hofmeister series for cations.

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Interest to the study of physicochemical properties of porphyrins and their metal derivatives is caused by the fact that complexes of metalloporphyrins play a decisive role in numerous biological systems [1, 2]. Owing to unique physicochemical properties of porphyrins and their derivatives, the fields of their application were considerably extended over the last years. One of such fields is ionometry, namely the creation of ion-selective electrodes with membranes containing complexes of porphyrins with various metals.

The important stage of the development of ion-selective electrodes is the choice of materials, which can be applied as membrane-active components in membranes selective to certain ions. The materials applied as membrane-active components in making polymeric plasticized membranes are commonly divided in two groups according to mechanisms of their operation: ion exchangers and neutral carrying agents. Anion exchangers are salts of organic bases: tetra-alkylammonium, phosphonium, and arsonium; cation exchangers, tetraborates of various metals. Selectivity of membranes based on ion exchangers is defined by a change in the solvation free energy upon the transfer of ions to be determined from aqueous solutions into a membrane phase. Values of selectivity characteristic of such membranes are arranged in so-called Hofmeister series [3] for anions $ClO_4^- > IO_4^- > SCN^- > I^- > NO_3^- > Br^- > NO_2^- > Cl^- > SO_4^{2-} > HPO_4^{2-}$ and for cations $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.

In the case of a specific interaction of an electrode-active substance with ions of a solution, membranes based on it exhibit selectivity inconsistent with the Hofmeister series. Aromaticity of the structure of metalloporphyrins, ability to form stable intramolecular complexes practically with all metals of the periodic system, and ability of metalloporphyrins to extra-coordination have served as a basis for using these compounds as electrode-active materials. Interactions characteristic for metalloporphyrins can be detected by a red shift of absorption bands in the electronic absorption spectra after contacting a porphyrin with an ion to be determined [4–7].

The possibility to apply in membranes of ion-selective electrodes metalloporphyrins containing the following metals as central ions has been investigated: Mn, Co, In, Al, Ti, Zr, Mo, and Hg [8–12]. Metalloporphyrins with metals of the group of lanthanides were scarcely studied [13, 14], however Messick et al. [13] have found that electrodes based on luteciumporphyrins show selectivity to salicylate ions. The study of electrode properties of membranes based on dysprosium- and luteciumtetrakis-*tret*-butylphthalocyanineacetate (Pc^tLuOAc, Pc^tDyOAc) has shown that the slope of the dependence $E = f(\log a_{\mathrm{sal}})$ is 41 mV/decade, i.e. it is slightly underestimated as compared to the theory [14].

The present work is devoted to the study of spectrophotometric and electrochemical properties of membranes based on holmium tetraphenylporphyrinchloride and is a prolongation of the works on studying physicochemical properties of porphyrins and their complexes with various metals carried out at the physical chemistry department of St. Petersburg State University [15–19].

Originality of porphyrin complexes with holmium in the oxidation state +3 is caused by the electron configuration $4f^{11}5d^06s^2$ of holmium atoms. Positively charged metal and divalent-negatively charged porphyrin (TPP^{2-}) form a uniform conjugate stable system of the metalloporphyrin with a unit positive charge ($HoTPP^+$).

The complex-forming ability of lanthanides is insignificant. It is connected with their electronic structure unfavorable for orbital hybridization, as the completing 4*f* shells are located very deep. The greatest ability to complex formation is exhibited by cerium in the most stable oxidation state +4, for which rather stable complexes are known: $[Ce(C_2O_4)_3]^{2-}$ and $[Ce(NO_3)_6]^{2-}$. Fluoride complexes are the most stable of halide complexes: $[MF_6]^{2-}$ (M = Ce and Pr) and $[MF_7]^{3-}$ (M = Ce, Pr, Tb), whereas for dysprosium only the complex $Cs_3[DyF_7]$ is known. Coordination number in complexes of lanthanides can vary within the range 6–12. In bromide and chloride complexes ($[PrCl_6]^{3-}$, $[NdBr_6]^{3-}$, and $[DyBr_6]^{3-}$) it is equal to six; in sulfate, thiocyanate, oxalate, and chromate complexes to eight ($[Sm\{CrO_4\}_2]^-$, $[Pr\{CrO_4\}_2]^-$); in iodide and bromate to nine ($[NdI_9]^{6-}$, $[Gd\{BrO_3\}_9]^{6-}$, and $[PrI_9]^{6-}$). No complexes of lanthanides with the coordination number 10 with monodentate ligands are known.

To elucidate the mechanism of substitution of OH^- group for extra-ligands in relation to pH of aqueous solutions, which are in contact with a membrane, we have taken absorption spectra of a HoTPPCl solution in chloroform that was beforehand brought to equilibrium with electrolyte aqueous solutions (two-phase titration) (Fig. 1).

It is seen from Fig. 1 that the optical density of a solution increases as its pH decreases, but at pH < 2 it starts to decrease, that can point to a porphyrin protonation and simultaneous releasing off the metal from the metalloporphyrin, i.e. the tetraphenylporphyrin complex with holmium is destroyed according to heterogeneous irreversible reaction (1).

$$\begin{array}{c} HoTPPCl(CHCl_2) + 2H^+_{\mathrm{sol}} \rightarrow H_2TPP(CHCl_2) + [HoCl]^{2+}_{\mathrm{sol}} \\ \downarrow +2H^+_{\mathrm{sol}} \\ H_4^{2+}TPP(CHCl_2) \end{array} \qquad (1)$$

The comparison of the HoTPPCl absorption spectrum at pH 1.8 with the free porphyrin (H_2TPP) spectrum (Fig. 2) confirms our assumption about existence of such process.

The analysis of the HoTPPCl spectrum taken in chloroform after a contact with a NaCl aqueous solution at pH 1.8 shows an explicit trend to increasing optical density of peaks at 515, 588, 647 nm, whereas the optical density at 553 nm decreases. The observed changes in spectral characteristics of the compound under study are fully compatible with the absorption spectrum of free porphyrin in chloroform.

Changes in the structure of the complex HoTPPCl can be also observed visually. All porphyrin complexes are colored. The solution of the complex of holmium tetraphenylporphyrinchloride in chloroform is of the brightly-pink color. On the titration by an acid the solution color is saved up to pH 2, at pH < 2 the color of the solution changes from pink to green. This circumstance also confirms the changes in structure of the metalloporphyrin under study.

At pH > 7 the ion exchange of an anion for the hydroxide ion [Eq. (2)] is possible in system (a bar from above hereinafter means belonging to an organic phase).

$$HoTPPCl + OH^- \rightarrow HoTPPOH + Cl^-. \qquad (2)$$

The apparent constant of the heterophase reaction is determined by formula (3).

$$[K] = \frac{[HoTPPOH][Cl^-]}{[HoTPPCl][OH^-]} \cdot \qquad (3)$$

We have constructed the plots of $\log (D_0 - D_x)/(D_x - D_l) = f(\mathrm{pH})$ for metalloporphyrin solutions in chloroform, and from their slopes have found the number of extra-ligand particles in the reaction and apparent constants of the heterophase reaction. For this

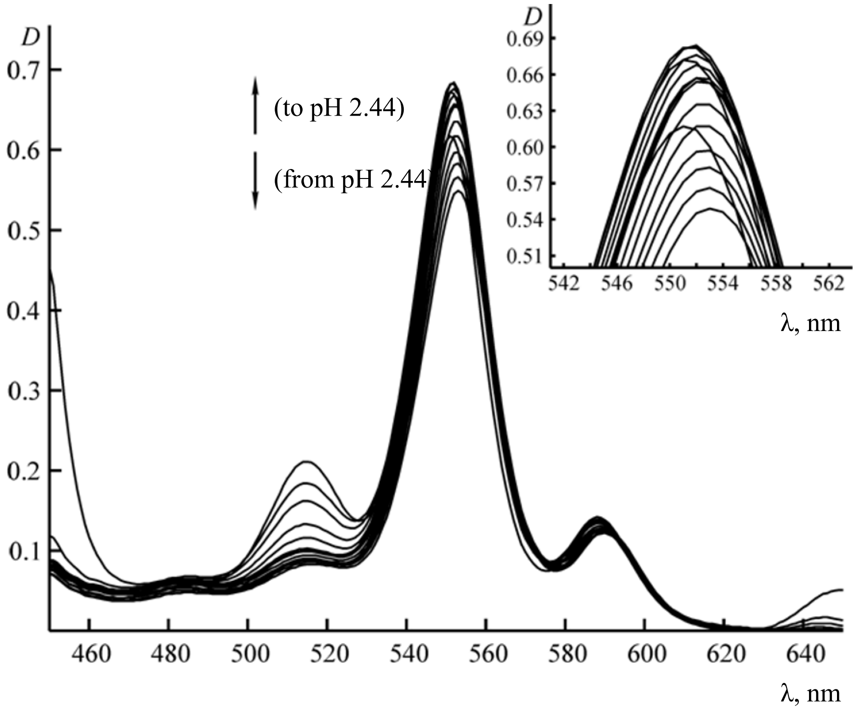

Fig. 1. Spectrum of HoTPPCl after contact with NaCl aqueous solutions with various pH values.

compound the number of extra-ligand particles in the reaction is 1.0, and the apparent constant is 3×10^{-9}. Using Eq. (4) connecting optical densities of n possible forms with pH and pK, we have calculated apparent constants of the heterophase reaction, the average value of which is 13×10^{-9}.

$$\log (D_0 - D_x)/(D_x - D_l) = n\text{pH} + \text{p}K. \quad (4)$$

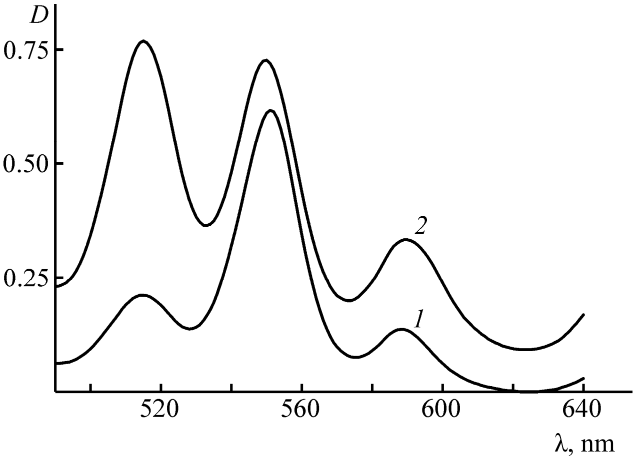

Fig. 2. (*1*) Spectrum of HoTPPCl after contact with a NaCl aqueous solution (pH 1.8); (*2*) spectrum of free porphyrin (H_2TPP).

Here D_0 is optical density of a metalloporphyrin in the beginning of titration (pH = 9.4), D_x is an experimental optical density, D_l is an optical density of a metalloporphyrin in the end of titration (pH = 2.4), and n is the number of extra-ligand particles in the reaction. The values of constants prove the correctness of conclusions on the occurrence of the reaction exchange of the anion for the hydroxide ion in the alkaline region.

The choice of a solvent-softener in membranes of ion-selective electrodes is very important. To determine the role of the solvent-softener in film membranes based on metalloporphyrins, in addition to the potentiometric analysis of membranes based on HoTPPCl, we have carried out the analysis of background membranes, i.e. the membranes containing only a solvent-softener and polyvinylchloride. The potential of membranes containing *o*-nitrophenyloctyl ether depends on pH of aqueous solution, i.e. this ether is not indifferent in the pH region under study and cannot be used as a solvent-softener. All the further experiments were carried out with dibutyl phthalate.

Electrodes with membranes based on holmium tetraphenylporphyrinchloride with dibutyl phthalate were held in a 0.1 sodium chloride solution within two days and then immersed in a 0.1 solution of NaCl +

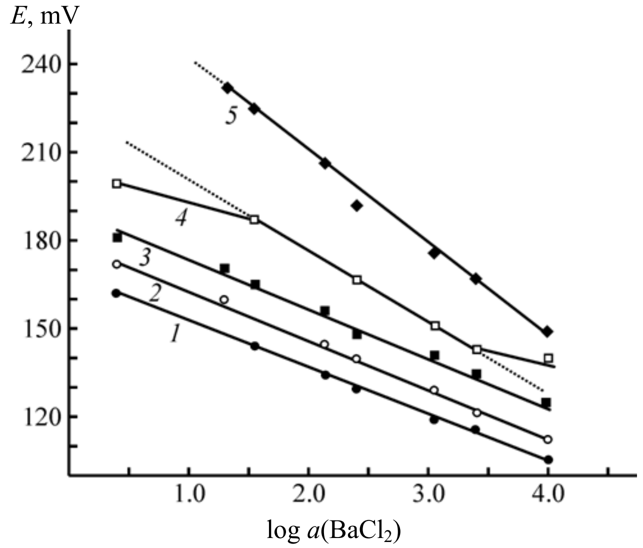

Fig. 3. EMF of cell (II) including membranes based on HoTPPCl and $BaCl_2$ solutions as a function of –log $a(BaCl_2)$ at various pH: (*1*) 5.7, (*2*) 6.2, (*3*) 7.0, (*4*) 7.4, (*5*) 7.7; α, mV/decade: (*1–3*) 16, (*4*) 24, (*5*) 27.

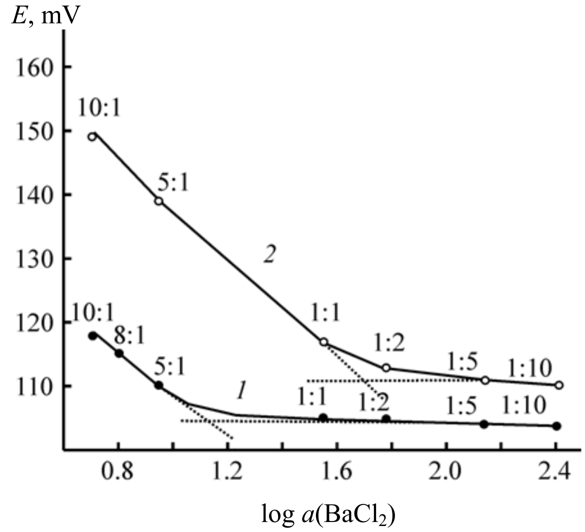

Fig. 4. EMF of cell (II) including membranes based on HoTPPCl and [$BaCl_2$ + MCl_2] solutions (*c* 0.1 M) as a function of –log $a(BaCl_2)$. M^{2+} = (*1*) Ca^{2+}, (*2*) Mg^{2+}. The ratio of molar concentrations of $BaCl_2$ and MCl_2 is specified above curves at each point.

TRIS with pH 9.4. The solution pH was reduced to 2.5 by gradual adding of hydrochloric acid in steps of 0.3–0.5. The region of the potential independence of pH for the electrodes ranges from 4 up to 9.

To clear up the limits of operation and entirety of electrode function realization, the behavior of electrodes based on holmium tetraphenylporphyrinchloride in solutions of various electrolytes was studied. Membrane electrodes based on HoTPPCl were calibrated by MCl_2 solutions ($M^{2+} = Ca^{2+}, Mg^{2+}, Ba^{2+}$) at various pH (Fig. 3).

It is seen from the values of slopes of the EMF dependence on $pMCl_2$ that the electrode function of membranes based on HoTPPCl increases as pH increases. As the concentration of OH^- ions increases, Cl^- ions in the complex with porphyrin are replaced by OH^- ions. As the O–H bond is polarized, reaction (5) of H^+ ions exchange for $CaOH^+$ ions, which are present in weakly alkaline solutions, is possible.

$$HoTPPOH_{mb} + CaOH^+_{sol} \rightarrow HOTPP\text{–}O\text{–}CaOH_{mb} + H^+_{sol}. \quad (5)$$

In an alkaline medium (pH 7–9) HoTPPCl can be used as a membrane-active component of electrodes selective to Ca^{2+}, Ba^{2+} cations (θ_{exp} 25–27 mV, range of the function fulfillment 10^{-4}–1.0 M).

Potentiometric selectivity coefficients is one of important characteristics of membranes. We applied the method of biion potentials and the method of mixed solutions for their determination. For the determination of selectivity coefficients IUPAC recommends the use of the method of mixed solutions as the most accurate, however we have obtained a good coincidence of log $[K]^{sel}(Ba^{2+}/M^{2+})$ values by both these methods. The method of biion potentials: log $[K]^{sel}(Ba^{2+}/Mg^{2+})$ 0.185 and log $[K]^{sel}(Ba^{2+}/Ca^{2+})$ –0.223; the method of mixed solutions: log $[K]^{sel}(Ba^{2+}/Mg^{2+})$ 0.196 and log $[K]^{sel}(Ba^{2+}/Ca^{2+})$ –0.314. The dependences of EMF on the activity of the primary ion at a constant activity of an interfering ion are presented in Fig. 4. The selectivity series obtained by the method of biion potentials and the method of mixed solutions for membrane electrodes based on HoTPPCl do not differ from the selectivity series for classical ion exchangers.

Electrodes based on HoTPPCl exhibit barium function in weakly alkaline and neutral solutions in the range of concentrations 10^{-4}–1.0 M and can be applied as ion-selective electrodes to the analysis of media with a complicated composition.

To study the dependence of the protonation of metalloporphyrins on pH of an aqueous solution contacting a metalloporphyrin solution in an organic solvent, we applied the method of two-phase spectrophotometric titration [20–22]. We have chosen chloroform as the organic solvent because it practically does not mix up with water, and at the same time it is sufficiently polar to provide solubility of ionic forms of the porphyrin under study.

The metalloporphyrin under study and background electrolyte, a solution of 0.1 M NaCl + TRIS, were placed in an electrochemical cell. The titration with HCl was carried out in steps of pH ≈ 0.5.

When the two-phase potentiometric acid-base titration was carried out pH of the aqueous phase was determined by means of galvanic cell (I).

$$\mathrm{Ag}\left|\mathrm{AgCl,\ KCl_{sat}}\right\vdots\ \mathrm{NH_4NO_{3\ sat}}\ \vdots\ \mathrm{NaCl + TRIS\ (0.1\ M)}\left|\ \text{glass electrode}\ \right|$$

$$\begin{array}{c}\text{(aqueous phase)}\\ \upharpoonleft\!\downharpoonright\\ \text{porphyrin solution}\\ \text{(organic phase)}\end{array}\qquad\text{(I)}$$

Then absorption spectra of the organic solution in the selected wavelength range were recorded. The criterion of reaching an electrochemical equilibrium was the constancy of the galvanic cell (I) EMF in time. After the complete separation of the water-organic mixture into layers optical density was measured on a spectrophotometer.

In addition to the study of HoTPPCl protonation and complex formation with its participation, a considerable part of the work was devoted to studying electrochemical properties of membranes based on holmium tetraphenylporphyrinchloride by means of the galvanic cell including membrane electrode (II).

$$\mathrm{Ag}\left|\mathrm{AgCl,\ KCl_{sat}}\right\vdots\ \mathrm{NH_4NO_3\ (0.1\ M)}\ \vdots\ \text{solution under study}\ \left|\ \text{membrane}\ \right|\ \text{0.01 M internal solution, AgCl}\ \left|\ \mathrm{Ag}\right.\qquad\text{(II)}$$

The potential of an ion-selective electrode is formed from the sum of all boundary potentials in a membrane penetrable only for ions X and Y [Eq. (6)].

$$[E]_{\mathrm{ISE}} = [E]^0 + \frac{2.303[R][T]}{[z]_{\mathrm{X}}[F]} \times \ln\left([a]_{\mathrm{X}} + [k]^{\mathrm{pot}}_{\mathrm{X,Y}}[a]_{\mathrm{Y}}\right) + [\varphi]_D. \qquad (6)$$

Here $[E]^0$ is the sum of all boundary potential jumps independent of X and Y concentrations or the standard value of the cell(II) EMF [23].

Entering of the ion $\mathrm{OH^-}$ in the metalloporphyrin structure affects electrochemical characteristics of membranes based on these products, which can also considerably change the slope of the $[E]$–(–log $[a]_{\mathrm{MA}}$) dependence and the range of the electrode function fulfillment for an ion to be determined. We determined a pH value of a solution under study in galvanic cell (III) and then measured the electrode potential at various pH in cell (II). Thus, we revealed the range where electrode potentials are independent of pH.

$$\mathrm{Ag}\left|\ \mathrm{AgCl,\ KCl_{sat}}\right\vdots\ \text{solution under study}\ \vdots\ \text{pH-metric electrode}\qquad\text{(III)}$$

To estimate the effect of interfering ions, we determine potentiometric selectivity coefficients by the method of biion potentials in 0.1 M solutions of the primary and interfering ions and also by the method of mixed solutions [24].

Selectivity coefficients determined by the method of biion potentials were calculated using Eq. (7). For singly charged ions Eq. (7) has form (8).

The method of mixed solutions [24] consists in measuring EMF of galvanic cell (II) in mixed solutions with a constant concentration of a foreign ion Y (background) and a variable concentration a of a primary ion X. The selectivity coefficient is determined by Eq. (9).

$$\log [K]^{\mathrm{pot}}_{\mathrm{X,Y}} = \frac{[E]_2 - [E]_1}{2.303[R][T][z]_{\mathrm{X}}[F]} + \left(1 - \frac{[z]_{\mathrm{X}}}{[z]_{\mathrm{Y}}}\right)\log [a]_{\mathrm{X}}, \qquad (7)$$

$$\log [K]^{\mathrm{pot}}_{\mathrm{X,Y}} = \frac{[E]_2 - [E]_1}{2.303[R][T][z]_{\mathrm{X}}[F]}. \qquad (8)$$

$$[K]^{\text{pot}}_{\text{X,Y}} = \frac{[a]_{\text{X}}}{[a]_{\text{Y}}^{z_{\text{X}} z_{\text{Y}}}}. \tag{9}$$

EXPERIMENTAL

The membranes studied in the work were made according to the common practice [25]; they represent polyvinylchloride films plasticized by solvents of various nature: dibutyl phthalate and *o*-nitrophenyl octyl ether. Holmium(III) tetraphenylporphyrinchloride (HoTPPCl) was used as an electrode-active material. Composition of the membranes: HoTPPCl 1 wt %, polyvinylchloride 33 wt %, and solvent-plasticizer 66 wt %. Disks of the diameter 7 mm were cut out of the resulting film and pasted to an end face of a polyvinylchloride tube serving as a membrane electrode frame.

In the work we used solutions of electrolytes (1×10^{-4}–1.0 M) prepared from salts of chemically-pure and special-purity grades by the weight (0.1–1×10^{-4} M) and volume dilution (1.0–0.1 M) methods. Solutions of MCl_2 (M^{n+} = Ca^{2+}, Mg^{2+}, Ba^{2+}) were used as electrolyte solutions. A constant pH of a contacting solution was maintained in each series. For this purpose solutions were prepared on the basis of tris (hydroxomethyl)aminomethane (TRIS). All measurements were carried out at room temperature (20±2°C).

Absorption spectra were recorded on a Shimadzu UV-1650PC spectrophotometer. The EMFs of galvanic cells were measured by means of a digital pH 150 pH-meter with the accuracy of ±0.5 mV.

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