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Basicity of *para*-Substituted Tetraphenylporphyrins Studied by Two-Phase Spectropotentiometric Titration

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Abstract—The basicity constants of a series of *para*-substituted tetraphenylporphyrins have been determined by two-phase spectrophotometric titration with pH monitoring in the chloroform–aqueous electrolyte solution system; the pH ranges of prevailing of the dication and the neutral forms of the porphyrins have been estimated. With introducing the donor substituents at the *para*-position of phenyl fragments of porphyrins, the compound basicity increases. Ionization constant of the pyrrole nitrogen atoms depends on the donor-acceptor properties of the substituents according to the Hammett equation. Basing on the derived dependence, theoretical basicity constants of the *para*-substituted porphyrins bearing strongly donor groups have been predicted.

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Acid–base equilibrium involving porphyrins in a variety of liquid phases have been discussed in a series of monographs [1–5] and reviews [6–8]. The majority of synthetic and natural porphyrins are well soluble in organic solvents, but only a few of them are water-soluble. Ionization properties of the water-soluble porphyrins in a wide range of the aqueous phase pH have been discussed in [6], whereas those of water-insoluble porphyrins in different organic solvents (acetonitrile, dimethylsulfoxide, methanol, etc) have been considered in [7, 8]. Nevertheless, the acid–base properties of porphyrins determined in the above-cited reports cannot be directly compared, as the acidity scale is specific for each of the solvents.

Ionization properties of porphyrins include the conditions of formation of their various ionic forms [2]. The porphyrins molecules are amphoteric, therefore, depending on conditions, their ionization occurs via different pathways [8]. In particular, they are capable of addition of one or two protons at the imine nitrogen atoms to form monocation H_3P^+ or dication H_4P^{2+} as well as of elimination of the pyrrole protons to form monoanion HP^- or dianion P^{2-}. The doubly protonated porphyrins are interesting as convenient models to study the specific features of the nonplanar macrocycles and the induced effects on the porphyrins reactivity.

In this work, the basic equilibriums (1)–(3) in the two-phase system (porphyrin solution in chloroform–aqueous electrolyte solution) were considered. The following *para*-substituted tetraphenylporphyrins were studied: $H_2TPP(4\text{-}OCOCH_3)_4$ (**I**), $H_2TPP(4\text{-}Cl)_4$ (**II**), H_2TPP (**III**), $H_2TPP(4\text{-}CH_3)_4$ (**IV**), $H_2TPP[4\text{-}C(CH_3)_3]_4$ (**V**), $H_2TPP(4\text{-}OCH_3)_4$ (**VI**).

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

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

$$H_4P^{2+} \leftrightarrow H_2P + 2H^+, K_{3,4}. \quad (3)$$

The following trends have been deduced from the study of porphyrins ionization [2]. The protonation constants K_3 and K_4 are close (within two orders of magnitude) in the case of many structurally different porphyrins. That means that the addition of the first proton does not change the basic properties of the molecule significantly. Being highly symmetrical, the porphyrin dications are extremely stable, in contrast to the monocations. In particular, the four-band electron absorption spectrum of H_2P changes into the two-band spectrum of H_4P^{2+} upon protonation. The total basicity constant $K_{3,4}$ strongly depends on the porphyrin structure.

The positions and intensities of the electron absorption bands are sensitive to the porphyrin molecule structure as well as to the presence of protonating and

complexing agents [9]. Protonation leads to distortion of the planar molecule structure and, thus, to elimination of both electronic and steric components of the macrocyclic effect. Hence, the ionization equilibriums constants can be determined via visible range spectrophotometry.

In this work, we took advantage of two-phase spectrophotometric titration with simultaneous monitoring of the aqueous phase pH [10–12] to study the porphyrins protonation.

The two-phase titration in the system of the aqueous electrolyte solution and the immiscible organic solvent has been applied to determine the acidity of the organic solvent used for extraction separation as well as to estimate the dissociation constants of water-insoluble acids and bases [13]. To properly describe the acid–base equilibriums in the two-phase system, the partitioning coefficients of the components between the phases should be taken into account besides the dissociation constants. Titration in the two-phase system is advantageous over the titration in nonaqueous medium: in the two-phase case, pH is determined in the equilibrium aqueous phase, hence, the activity of protons and other components could be easily calculated. The instrumental methods of measurement of the aqueous solutions pH have been thoroughly studied and standardized.

Titration in nonaqueous solvents has allowed determination of the equilibrium constants, otherwise nonmeasurable. In practice, the nonaqueous titration is associated with a number of complications. Firstly, the residual water content in the nonaqueous solvent should be accurately determined. Secondly, the protons activity in the nonaqueous medium should be calculated. Finally, the glass electrode behavior in nonaqueous media is strongly affected by its preconditioning.

In this work, in the course of two-phase titration, the indicator and the reference electrodes were immersed into the aqueous phase, thus eliminating the above-mentioned complications. The basicity constants of a series of *para*-substituted tetraphenylporphyrins in chloroform solution were determined by processing the titration results. Determination of the pH ranges of domination of the cation forms of the porphyrins constituted an important part of the work, and the ways to extend that range by chemical modification of the phenyl rings were developed.

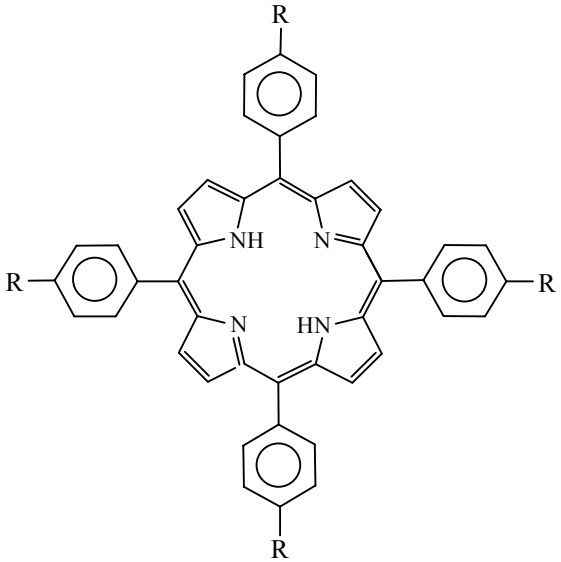
The linear Hammett equation (4) was used to quantitatively describe the effects of electron-donating or electron-accepting groups on the reactivity of porphyrins, in particular, to calculate the basicity constants of a series of structurally similar porphyrins [14].

$$\log (K_X/K_{un}) = \sigma\rho, \quad (4)$$

where K_{un} and K_X, constants of equilibrium involving the unsubstituted compound and the X-substituted compound, respectively; σ, the constant reflecting the ability of X to change the electron density at the reactive center as compared to that of hydrogen atom; ρ, reaction constant reflecting sensitivity of the studied process towards the solvent change. ρ is generally determined by the process type, temperature, and the substituent nature.

The shape and intensity of the electron absorption bands reflected the state of π-electron cloud of the porphyrin molecule and, therefore, the molecular structure [9]. Upon modification of porphyrin macrocycle, the general features of electron absorption spectra were preserved.

Absorption spectra of solutions of H_2TPP (**III**) as function of $NaClO_4$ aqueous solution pH are shown in Fig. 1; the spectra of *para*-substituted tetraphenylporphyrins were similar. When the solution of tetraphenylporphyrin was equilibrated with the aqueous acidic solutions, the porphyrin spectrum was changed as compared to that of the pure solution in chloroform.



R = $OCOCH_3$ (**I**), Cl (**II**), H (**III**), CH_3 (**IV**), $C(CH_3)_3$ (**V**), OCH_3 (**VI**).

Table 1. pH ranges of dications existence and the experimental values of the total acidity constant of porphyrins **I**–**VI**

Comp. no.	Substituent	Range of the dication existence, pH	σ_{para}	$pK_{3,4}$, ±0.1
I	*p*-$OCOCH_3$	<0.1	+0.390	1.9
II	*p*-Cl	<0.3	+0.227	2.9
III	H	<1.1	0	4.3
IV	*p*-CH_3	<1.4	–0.170	5.2
V	*p*-$C(CH_3)_3$	<1.5	–0.197	5.2
VI	*p*-OCH_3	<2.2	–0.268	6.4

Table 2. The total basicity constants of porphyrins with strong donating *para*-substituents calculated with the Hammett equation

Comp. no.	Substituent	σ_{para}	$pK_{3,4}$, ±0.1
VII	OH	–0.370	6.7
VIII	$OCH_2C_6H_5$	–0.42	7.0
IX	$NHNH_2$	–0.55	7.8
X	$NHCH_2CH_3$	–0.61	8.2
XI	NH_2	–0.66	8.5
XII	$N(CH_3)_2$	–0.83	9.6
XIII	$NHCH_3$	–0.84	9.7

In particular, the *I* band was sharply enhanced and slightly shifted towards longer wavelengths, whereas the band *IV* almost vanished. Such spectral changes evidenced about formation of the H_4P^{2+} dications. With increasing pH of the equilibrated aqueous phase, the intensity of band *I* decreased, being shifted towards short wavelengths, and the intensity of band *IV* increased, due to deprotonation reaction (3).

The H_3P^+ species were not spectrally detected, therefore, indeed the K_3 and K_4 values were relatively close, as was marked in [2].

The absorbance *D* of solutions of porphyrins in chloroform as function of pH of the equilibrated aqueous solution of $NaClO_4$ is shown in Fig. 2; in the cases of all the studied porphyrins, the curves revealed steep decrease at certain point with increasing pH. The pH ranges of existence of dication forms of the porphyrins **I**–**VI** are given in Table 1; the range strongly depended on the nature of the peripheral substituent introduced at the porphyrin cycle. The electron donors [CH_3, $C(CH_3)_3$, and OCH_3] extended the range of dominating of the dication form, whereas the effect of electron acceptors ($OCOCH_3$ and Cl) was the opposite. Introduction of *para*-Cl substituents (known for the negative inductive effect –*I* and weak conjugative effect +*C*) at phenyl rings of H_2TP weakened the basic properties of the compound. Vice versa, introduction of the electron donor groups [CH_3, $C(CH_3)_3$, and OCH_3] significantly enhanced the compound basicity. Noteworthily, $H_2TPP(4\text{-}OCH_3)_4$ was significantly more basic than $H_2TPP[4\text{-}C(CH_3)_3]_4$ due to the strong +*C* effect of the substituents.

Processing of the two-phase titration spectra [11] yielded the basicity constants $pK_{3,4}$ of the *para*-

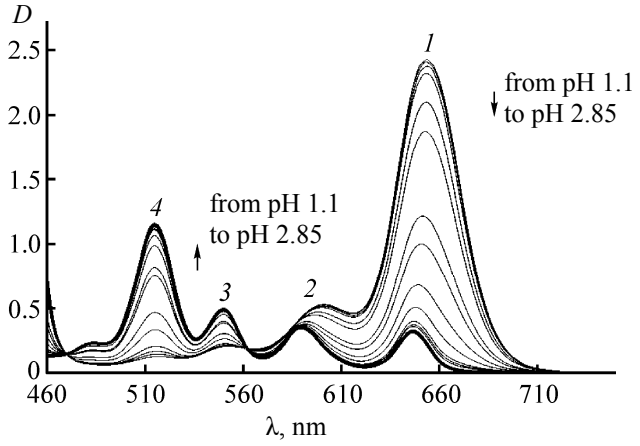


Fig. 1. Electron absorption spectra of H_2TPP (**III**) as function of pH of the equilibrium aqueous solution of $NaClO_4$.

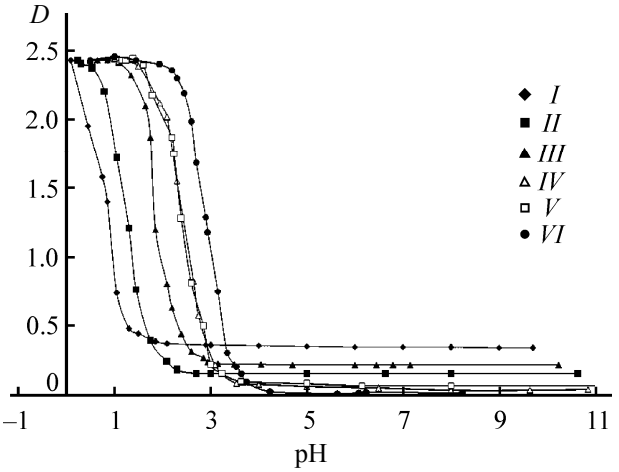


Fig. 2. Absorbance of *para*-substituted tetraphenylporphyrins (maximum of the *I* band) as function of pH of the equilibrium aqueous solution of $NaClO_4$.

substituted tetraphenylporphyrins **I–VI**. For the calculation, the absorbance at the maximum of the band *I* was used.

$$pK_{3,4} = 2pH - 2\log a(ClO_4^-) - \log [(D_0 - D_x)/(D_x - D_l)], \quad (5)$$

where D_0, absorbance of the porphyrin in dication form; D_l, absorbance of the neutral porphyrin form; D_x, absorbance of the mixture of the forms. The Eq. (5) accounted for the absence of specific monocation bands in the spectra.

Basicity constants of the studied *para*-substituted tetraphenylporphyrins are collected in Table 1.

The studied porphyrins contained the same *para*-substituents in the four phenyl rings; therefore, the 4σ parameter could be used as the total substituent constant [15]. The Hammett equation (4) was thus transformed into the Eq. (6).

$$\log (K_X/K_{un}) = 4\sigma\rho. \quad (6)$$

The experimental basicity constants plotted in the corresponding coordinates are shown in Fig. 3. As seen from Fig. 3, the constants were well fitted with Eq. (6), the correlation coefficient being of 0.99. From the slope of the fitting line, the ρ value equaled 1.6; the positive slope indicated that introduction of the electron accepting substituents suppressed the compound protonation. On the contrary, the donor substituents suppressed the compound deprotonation, and the pH range of the dication form existence was broadened. The absolute value of ρ reflected the degree of change of the electron density upon transformation of the dication form into the neutral one.

Using the Hammett equation, the basicity constants of the porphyrin containing other *para*-substituents could be calculated using Eq. (6), the tabulated σ values [16], and the determined ρ = 1.6 value.

We calculated the basicity constants $pK_{3,4}$ values for tetraphenylporphyrins containing the strongly donor substituents; the calculated basicity constants are collected in Table 2.

As expected, the broader range of dication existence was typical of the most basic porphyrins.

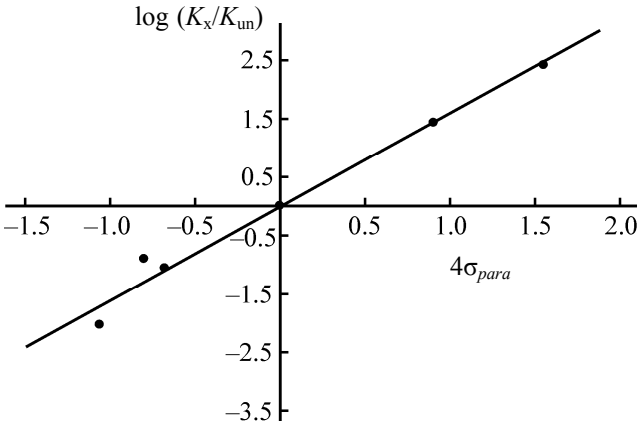


Fig. 3. The Hammett plot of the basicity constants of *para*-substituted tetraphenylporphyrins.

Therefore, such compounds can be potentially efficient as the membrane-active component of the anion-selective electrodes.

EXPERIMENTAL

The studied *para*-substituted tetraphenylporphyrins were prepared at Laboratory of Physical Chemistry of Electrolytes, St-Petersburg State University.

The basics of application of two-phase spectrophotometric titration to study the acid–base properties of porphyrins are to be found in [10–12]. In this work, chloroform was used as the organic phase in two-phase spectrophotometric titration. Chloroform was immiscible with water and allowed for sufficient solubility of the ionic forms of the studied porphyrins.

Experiments were performed at 22±1°C. Porphyrin (dissolved in chloroform) and the background $NaClO_4$ solution were placed in the electrochemical cell; titration was started at pH of 0.25.

pH of the aqueous solutions in contact with the organic phase was determined with the voltaic cell.

pH of the aqueous solutions was measured with I-130 ion meter (ESL-41G-07 glass electrode, calibrated with the reference buffer solutions). NaOH was used as titrant, the titration step was of pH ~ 0.3.

AgCl | AgCl, KCl(sat.) | NH_4NO_3(sat.) | $NaClO_4$(1 M.) | glass electrode |

(aqueous phase)

⇅

Porphyrin solution

(organic phase)

The interphase equilibrium state was judged from the constancy of the voltaic cell electromotive potential in time. After complete aliquation of the aqueous-organic mixture, the absorbance of the organic phase was determined with Shimadzu UV-1650 spectrophotometer.

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