ACID–BASE INTERACTION OF TETRAAZAPORPHIN IN ORGANIC SOLVENTS

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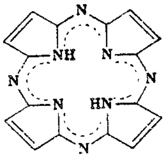
The state of free tetraazaporphin in proton-donor media was studied.

The spectroscopy of acid–base forms of porphyrins are discussed in monograph [1]. The thermodynamics of the acid–base interaction and general problems of protonation of the aza-derivatives of porphyrins (phthalocyanines, etc.) are discussed in monograph [2]. Analysis of acid–base processes (in particular in organic solvents) with the participation of polycentered conjugated bases, such as the aza derivatives of aromatic compounds, shows that the simple concept of proton transfer according to Brφnsted [3] is insufficient. Only multistage representations of the acid–base process [4, 5] may lead to a correct interpretation of the results. Ignoring H-association and ionic association as important stages of the acid–base process leads to an incorrect and simplified interpretation of the acid–base reaction of phthalocyanines [6-11].

In the present work, the characteristics of the acid–base reaction of tetraazaporphin (I) with H_2SO_4 in an organic solvents medium are studied.



I

Data on the electronic absorption spectra (EAS) of tetraazaporphin (H_2TAP) (Figs. 1, 2) show that in a neutral solvent (DMSO), in a weakly proton-donor solvent (CH_3COOH), and in a series of acidic and strongly acidic solutions with an increasing value of the Hammet's acidity function (H_0), H_2TAP forms several spectral forms. To interpret these, we must turn to the general theory of acid–base interaction and to the main concepts on the structure and properties of aromatic multicentered bases. According to the Brφnsted definition [3], the acid–base interaction is determined by mobility of a proton, and is accompanied by its transfer from an acid to a base. The degree of this transfer was not stipulated by Brφnsted. Therefore, great difficulties arose on transition from aqueous to nonaqueous solutions of acids and bases. As a result, the formation of several products with different types of acid–base interaction between acid HA and base B was not taken into account. This led to errors in processing the experimental data as, for example, in the HA–phthalocyanines systems [6-11]. Shatenshtein [4] and Izmailov [5] considered the complexity of the acid–base reactions and treated the acid–base interaction as a multistage process:

$$\underset{\mathrm{IA}}{\mathrm{B}:} + \mathrm{HA} \rightleftarrows \underset{\mathrm{IIA}}{\mathrm{B}:\ldots\overset{\delta+}{\mathrm{H}}\overset{\delta-}{\mathrm{A}}} \rightleftarrows \underset{\mathrm{IIIA}}{\overset{\delta+}{\mathrm{BH}}\ldots\overset{\delta-\,\mathrm{solv}}{\mathrm{A}}} \rightleftarrows \underset{\mathrm{IVA}}{\mathrm{BH}^{+}_{\mathrm{solv}}} + \mathrm{A}^{-}_{\mathrm{solv}}, \tag{1}$$

The end result of this process depends on the electronic and geometrical structure of the acid and base, and also on the solvation features of anion A^- and cation BH^+, determined by the nature of the solvent. The role of the solvent is particularly important at the ionization stage, at which an ionic protonated form IVA is formed. Phthalocyanines and azaporphyrins are very weak based as the result of n–π-conjugation of the N-orbitals with the π-system of the macrocycle [2]. In their case, a multistage process (1) should predomi-

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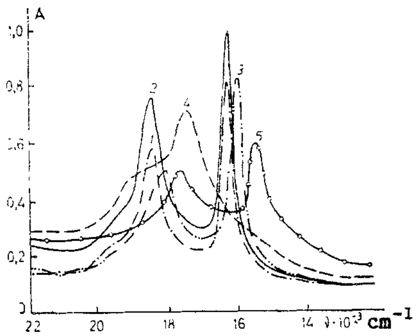


Fig. 1

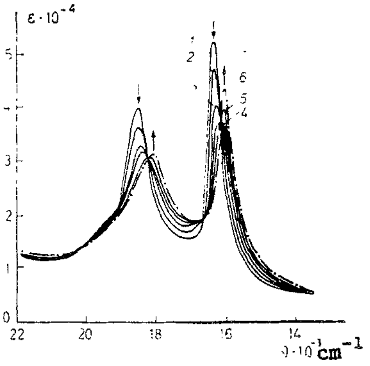


Fig. 2

Fig. 1. Electronic absorption spectrum of tetraazaporphin: 1) DMSO; 2) in 100% CH_3COOH; 3) 0.03% H_2SO_4 in CH_3COOH (H_0 = −1); 4) 45% H_2SO_4 in CH_3COOH (H_0 = −5.6); 5) 100% H_2SO_4 (H_0 = −11.9).

Fig. 2. Electronic absorption spectrum of tetraazaporphin in a H_2SO_4–C_2H_5OH binary solution: 1) 100% C_2H_5OH; 2-6) at acidities of medium H_0: +0.60, −0.05, −0.25, −0.61, and −0.92, respectively.

nate in a medium of weakly ionized solvents (carboxylic acids, esters, ketones, etc.) For the same reason, a strong interaction of phthalocyanines and related molecules of complete protonation type is not possible with more than one more proton. The nitrogen atoms remaining in the BH^+ ion may with HA give weak H-associated of type IIa only and, possibly, in rare cases, acidic nonionic associates of type IIIA.

In an analysis of spectroscopic data, we should bear in mind a possible increase (by 5-8 orders of magnitude) of the basicity of the excited states of molecules of bases with a conjugated system of π-electrons, which includes hetero atoms [12]. As a result of the $\pi \rightarrow \pi^*$-electronic excitation, the n–π-conjugation practically disappears in these bases. Therefore, during photoexcitation, the H-associate or acid solvate may convert into a protonated form:

$$B{:}\ldots HA \xrightarrow{h\nu} (B{:}\ldots HA)^* \longrightarrow (BH^+)^* + A^-. \qquad (2)$$

However, in weakly solvated (weakly coordinated) solvents, also under these conditions, no ionic form BH^+ can be formed [13], but an ionic pair $(BH^+)^*\ldots A^-$ [12].

The acid–base properties of the excited molecules, and hence their electronic spectra, will change depending on the character of the medium in which the H-associates exist, and on the energy level into which the π-electron is excited. Decrease in the basicity or acidity of the excited bases and acids is also possible [12].

Therefore, any comparison of the constants of the acid–base interaction obtained by the thermodynamic method [13] for the ground states of the molecules with those obtained by the spectroscopic method for molecules with possible phototransfer of a proton, must be made with caution.

In the presence of a strong proton-donor (H_2SO_4) in media from weakly acid (H_0 = 0) to strongly acid (H_0 = −11.9), tetraazaporphin forms four spectrally different forms with λ_I = 613, 625, 571, 643 nm (Fig. 1), irrespective of the nature of the main solvent (CH_3COOH, C_2H_5OH). The form with λ_I 613 nm corresponds to a porphin ligand H_2TAP and symmetric acid solvate $H_2TAP(HA)_n$ in weak acids (RCOOH).

When interpreting the acid forms of H_2TAP, in addition to the above considerations, we take into account the following factors. Thermodynamic and electronic absorption spectroscopy methods [14] showed that in aqueous H_2SO_4 (8-18.8 M), chlorosulfonic acid and oleum, phthalocyanine and its complexes with metals (phthalocyanine is also a tetraazaporphyrin) form one single singly-protonated form under these conditions. This form, produced under the favorable conditions of a strongly polar ionizing medium has a maximally possible polarization, shown by the maximally long-wave 100-120 nm shift of the first absorption band on

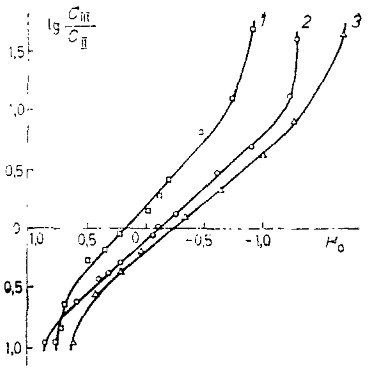


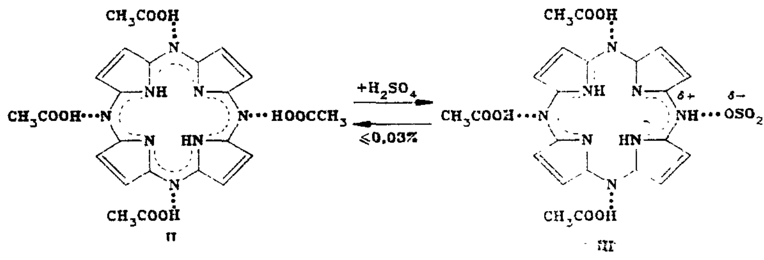
Fig. 3. Titration curves for formation of H-associate of tetraazaporphin III in H_2SO_4–CH_3COOH (1), H_2SO_4–C_2H_5OH (2), and $SnCl_4$–CH_3COOH (3) medium.

transition from the nonprotonated form to a singly protonated form of phthalocyanine and its complexes. The formation of doubly and thrice and more protonated forms, impossible because of electronic and energetic concepts, would lead to a short-wave shift of the first absorption band, compared with the monoprotonated form, as a result of contrapolarization of the chromophore by several H^+ auxochromes and shortening of the π-electron transfer path [12].

A characteristic feature of the electronic structure of phthalocyanines [14] is the extraordinarily strong n–π-conjugation of the filled φ_N-orbitals of the nitrogen atoms with the vacant ψ_{π}*-orbitals. Therefore, even a single protonation of the N atom is energetically unfavorable, and occurs only in strongly acid media (aqueous H_2SO_4, oleum, $ClSO_3H$, etc.). It is assumed that the (+)-charge is distributed over the π-system of the macrocycle, especially over the nitrogen mesoatoms. Further protonation of the bridging nitrogen atoms is difficult because of the increase in n–π-conjugation and accumulation of a charge ($\delta^+ \geq 0.1$) on the remaining nitrogen atoms.

Tetraazaporphin I and its complexes, like phthalocyanines, are aromatic macrocycles [15], have a planar structure of the 16-membered chromophore, and are characterized by a strong n–π-conjugation and very low basicity. Hence, in the presence of several acid–base forms of tetraazaporphin in a solvent–strong acid medium, the ultimate acid form may, as in phthalocyanine, be a singly protonated form. A maximal bathochromicity of the λ_1 will correspond to this in the electronic absorption spectrum. Because the π-system of H_2TAP and MTAP is shorter than that of phthalocyanines, the $\Delta\lambda_1$ shift during protonation should be much shorter.

The above shows that the following interpretation of the acid forms of H_2TAP in CH_3COOH (C_2H_5OH)–H_2SO_4 medium is most probable. When small amounts (0.03%) of H_2SO_4 are introduced into a solution of H_2TAP in acetic acid, the acid solvate (II) with λ_1 613 nm converts into an H-associate (III) with λ_1 625 nm (Fig. 1, 2).

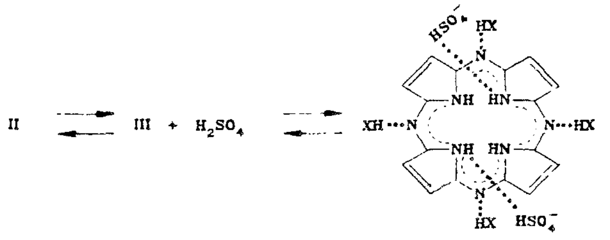


(3)

The value of pK_{III}, determined by spectrophotometric titration (Fig. 3) using the Hammet's equation (5), in H_2SO_4–CH_3COOH and H_2SO_4–C_2H_5OH media is equal to -0.15 ± 0.03 and -0.11 ± 0.03, respectively. This form is stable and does not undergo degradation. This fact, and also the high values of pK_{III}, confirm the supposition that form III is an H-associate only. It has a spectral affinity to coordinated compounds $H_2TAP \cdot SnCl_4$ existing in both aprotic solvent, DMFA (λ_1 629 nm) and a weakly-donor solvent CH_3COOH (λ_1 625 nm). In a CH_3COOH–$SnCl_4$ medium, a stability constant $pK_{st} = -0.18 \pm 0.07$ was determined for this compound. Hence, the two particles are associates, with similar strength and character of interaction.

The next two forms are more acidic, undergo a rapid degradation, and, therefore, an accurate value of their pK was not found. With increase in the H_2SO_4 concentration in $CH_3 \cdot COOH$ to 45%, an acid form IV is preferentially formed with λ_I 571 nm and a relatively strong continuous absorption in the 500- to 600-nm region. This shows that several acid solvates of the particles are present at equilibrium. Form IV has an approximate pK_{IV} value of the order of −4 to −5. The spectral similarity of this form with those of metal complexes indicates that it is centrally symmetric and that in this form two central tertiary nitrogen atoms react with an acid (4).

Salt formation in the center probably does not lead to the formation of a dication, as is usually assumed for an aqueous solution of porphyrins proper [2]. In nonaqueous media, the acid–base process practically always ceases at the H-associates or ion–ion associates [13]. Under the conditions of formation of IV, large amounts of CH_3COOH do not favor the dissociation of the ionic associates.



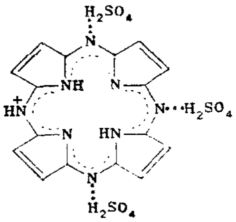
IV (4)

The formation of a centrally symmetric dication H_4TAP^{2+} (like H_4Pc^{2+}) is energetically unfavorable, since it would lead to the deviation of two pyrrole rings from the plane. This is possible in porphyrins, and not very probable in more aromatic tetraazaporphyrins [2]. It can be assumed that as a result of the accumulation of positive charges on the macroring atoms in form IV, the peripheric nitrogen atoms form only a very weak hydrogen bond with acid HX (CH_3COOH, H_2SO_4, HSO_4^-).

With further increase in the H_2SO_4 concentration in the binary mixture from 50 to 100%, the protonating and ionizing ability of the solvent strongly increases. It is possible that under these conditions form IV cannot transform into the centrally symmetric dication H_4TAP^{2+} for the above reason, and a new form appears in the equilibrium, the acid solvate of singly protonated form V:

$$\mathrm{II} \rightleftharpoons \mathrm{III} \rightleftharpoons \mathrm{IV} \rightleftharpoons \mathrm{V}$$

with λ_I 643 nm and a tentative value of pK_V of the order of magnitude of −7. Its averaged composition is illustrated by formula V. The stability of this form was studied in [16]. As a result of the low polarizability of π-electron cloud, the $\Delta\lambda_I$ in form V is not more than 30 nm instead of 120 nm in H_2Pc.



V

EXPERIMENTAL

Tetraazaporphin, 100% sulfuric acid, anhydrous acetic acid were prepared by the method in [16]. Absolute ethanol was prepared according to [17]. Grade c.p. $SnCl_4$ was additionally distilled. The content of water in solvents was controlled by titration by the Fischer method, and did not exceed 0.01%. A known amount of tetraazaporphin was dissolved in media on a Specord UV-vis spectrophotometer. The spectroscopic data were processed by the method in [18]. The spectrophotometric titration curves (Fig. 2) were plotted in the $\log(C_{III}/C_{II}) = f(H_0)$ coordinates. The values of the Hammet's acidity function were taken from [19]. The acid–base interaction constants pK_{III} were determined from the equation

$$pK_{III}=H_0+\lg(C_{III}/C_{II}) \quad (5)$$

LITERATURE CITED

1. G. P. Gurinovich, A. N. Sevchenko, and K. N. Solov'ev, Spectroscopy of Chlorophyll and Related Compounds [in Russian], Nauka i Tekhnika, Minsk (1968).
2. B. D. Berezin, Coordination Compounds of Porphyrins and Phthalocyanine [in Russian], Nauka, Moscow (1978).
3. I. N. Brφnsted, Rec. Trav. Chim. Pays-Bas, 42, 718 (1923).
4. A. I. Shatenshtein, Theory of Acids and Bases [in Russian], Goskhimizdat, Moscow—Leningrad (1949).
5. N. A. Izmailov, Electrochemistry of Solutions [in Russian], Khimiya, Moscow (1976).
6. A. H. Ahrens and Kuhn, Z. Phys. Chem., 37, 1 (1963).
7. S. Gaspard, M. Verdaguer, and R. Viovy, Compt. Rend., 277, 821 (1973).
8. S. Gaspard and R. Viovy, J. Chimie Physique, 78, 851 (1981).
9. S. S. Iodko, O. L. Kaliya, M. G. Gal'pern, V. N. Kopranenkov, O. L. Lebedev, and E. A. Luk'yanets, Koord. Khim., 8, 1025 (1982).
10. O. L. Kaliya, O. L. Lebedev, and E. A. Luk'yanets, Koord. Khim., 5, 611 (1979).
11. A. S. Akopov, N. Yu. Borovkov, and I. V. Surov, in: 4th Conference on Chemistry and Use of Porphyrins, Summaries of Lectures [in Russian], Erevan (1984), p. 6.
12. A. N. Terenin, Photonics of Molecules of Dyes and Related Organic Compounds [in Russian] Nauka, Moscow (1967).
13. S. P. Miskidzh'yan and A. D. Garnovskii, Introduction to Modern Theory of Acids and Bases [in Russian], Vysshaya Shkola, Kiev (1979).
14. B. D. Berezin, Zh. Fiz. Khim., 321 (1965).
15. Porphyrins: Structure, Properties, Synthesis, N. S. Enikolopov (ed.) [in Russian], Nauka, Moscow (1985).
16. O. G. Khelevina, P. A. Stuzhin, and B. D. Berezin, Khim. Geterotsikl. Soedin., No. 7, 932 (1984).
17. Organicum, Vol. 2 [translated from German], Mir, Moscow (1979), p. 376.
18. A. Albert and E. Sergent, Ionization Constants of Acids and Bases [Russian translation], Khimiya, Moscow—Leningrad (1964).
19. Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions [in Russian], Vol. 5 (1), V. A. Palm (ed.), VINITI, Moscow (1978).