ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 3, pp. 602–606. © Pleiades Publishing, Ltd., 2011.
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Determination of Acidity of Di-, Tri-, and Tetraazaporphyrins in Dimethyl Sulfoxide–Potassium Cryptate Medium

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Received April 12, 2010

Abstract—Acidic properties of 10,20-diaza-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-hexylporphyrin, 2,7,12,17-tetra-*t*-butyltetrabenzo-5,10,15-triazaporphyrin and octa(*n*-amyloxy)phthalocyanine in the system of dimethyl sulfoxide–potassium cryptates (DMSO-K[222]OH) at ambient temperature was investigated by the method of spectrophotometric titration. The porphyrins in the DMSO–K[222]OH medium were shown to dissociate sequentially forming mono- and dianions in two steps. The concentration ranges of existence of the anionic forms and the acidity sequence of the studied *meso*-aza-substituted porphyrins were investigated.

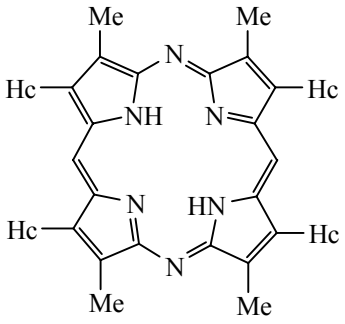
DOI: 10.1134/S1070363211030285

An exclusively important role of anions in chemical biology is defined by their role in the cell metabolism, osmotic balance and the most enzymatic transformations [1–3]. Many anions have large ionic radii compared to the cations and, consequently, less effective charge, which is a definite obstacle to use them for the creation of ion receptors. A solution to this issue would be creation of large molecular assemblies with the properties of the anions, and deprotonated forms of porphyrins obey this requirment.

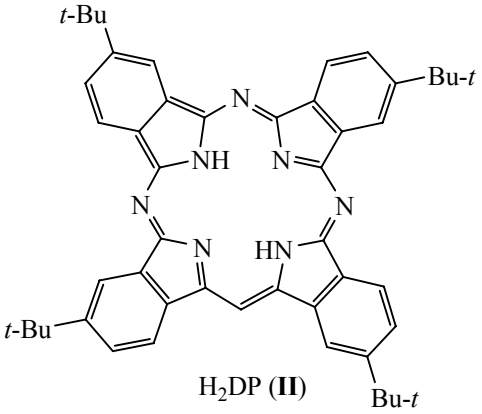
Aza-porphyrins in this regard are of particular interest because of the presence of nitrogen atoms in the *meso*-position of the macrocycle (from one to four), converting porphyrin into organic acid, whose strength depends on the nature of the solvent. Due to the electronegativity of heteroatoms that leads to the extension of the aromatic system, the aza-bridges increase the stability of the aza-porphyrin anionic forms compared with the porphyrins.

The determining factor in the study of anionic interaction is the choice of environment. It is known [4, 5] that there are the ranges of acidity where molecules are in the anionic form. Depending on the nature of the solvent, and hence on the respective scale of acidity, these ranges may vary significantly. In nonpolar solvents the creation of anionic form is impeded by the influence the counterion and by weak solvation. In polar solvents, the solvation of the counterion hinders the deprotonation. The analysis of the literature and our own data on the study the acid properties of macrocycles [6, 7] shows that the most promising solvent for the creation of the conditions of chemical transformations is dimethyl sulfoxide (a dipolar aprotic solvent). In the present study we investigated the acidic properties of 10,20-diaza-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-hexylporphyrin (**I**), 2,7,12,17-tetra-*tert*-butyltetrabenzo-5,10,15-triazaporphyrin (**II**), and octa(*n*-amiloxy)phthalocyanine (**III**) in the system dimethyl sulfoxide–potassium cryptate (DMSO–K[222]OH) at ambient temperature. We have found that porphyrins in the DMSO–K[222]OH medium dissociate in two steps forming sequentially mono- and dianions. The concentration range of existence of the anionic forms and the acidity sequence of *meso*-substituted azaporphyrins **I–III** were determined.

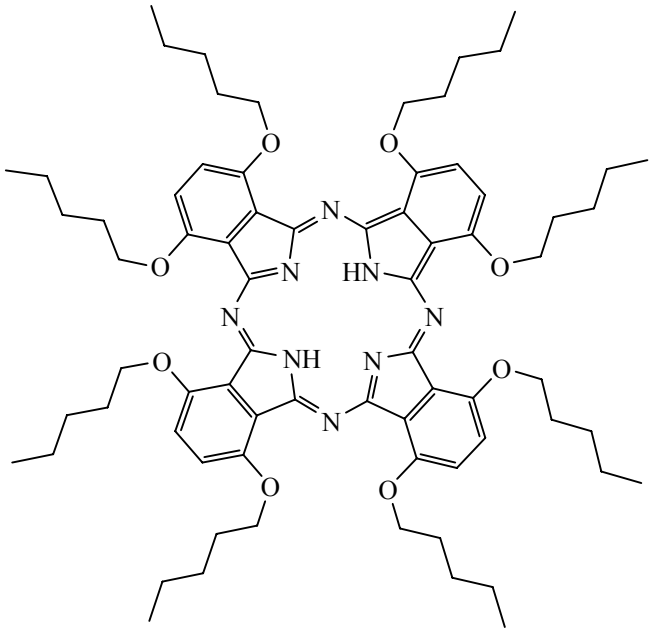
The investigation of acid properties of azaporphyrins (**I–III**, H_2R) was performed by spectrophotometric titration in the system DMSO–K[222]OH at ambient temperature. The titration was carried out in DMSO medium by the solution of K[222]OH prepared on the basis of DMSO with the concentration of 0.03 M. The criteria of selection of this system have been described in more detail in [8].



H_2DP (**I**)



H_2DP (**II**)



$H_2PC(OAm)_8$ (**III**)

During the titration of H_2DP by the system DMSO–K[222]OH (Figs. 1–3), in the EAS the successive formation of HP^- and P^{2-} forms was registered [Eqs. (1), (2)], as evidenced by two sets of isosbestic points formed in the outer acidity regions of the porphyrin solutions. The corresponding titration curve (Fig. 4) exhibits two stages, to each of which corresponds its own set of spectral curves in the EAS. At the increase in the pH of the solutions due to the increase in the content of hydroxide ions, in the EAS of compound **I** a strong blue shift is observed of the bands with λ_{max} 552, 630, and 771 nm to 562, 599, and 630 nm, respectively, in the first step of the acid dissociation and further blue shift of these bands to λ_{max} 401, 599, and 713 nm respectively in the second step of the acid dissociation. At the same time in the EAS the narrowing and significant growth in intensity is observed of the absorption band at 599 nm (Table 1). After determination of the inflection points on the titration curve (Fig. 4) as described in [9] the deprotonation processes in the system DMSO–K[222]OH were divided into separate stages (Figs. 2 and 3) and by the formula (3) the corresponding constants were calculated (Table 2).

$$H_2P \rightleftarrows HP^- + H^+, k_{a1}, \quad (1)$$

$$HP^- \rightleftarrows P^{2-} + H^+, k_{a2}, \quad (2)$$

$$\log k = n\log c - \log (\mathrm{Ind}), \quad (3)$$

where k is the dissociation constant of the first or second stage, respectively Eqs. (1), (2); Ind is the indicator ratio $(H_2P)/HP^-$ for the first stage and the $(HP^-)/(P^{2-})$ for the second; c is the analytical value of the concentration of potassium cryptate in the solution, M, n = 1 (the number of hydroxy groups). The error in

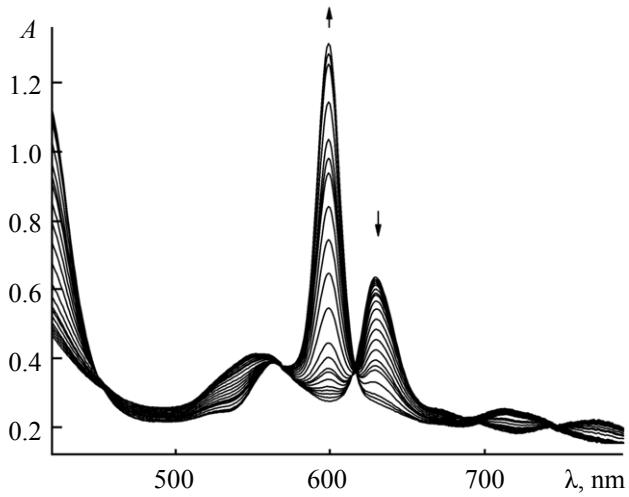


Fig. 1. Spectrophotometric titration of compound **I** (C_{porph} = 6.30×10^{-4} M) in the system DMSO–K[222]OH at the (K[222])OH concentration from 0 to 1.60×10^{-3} M.

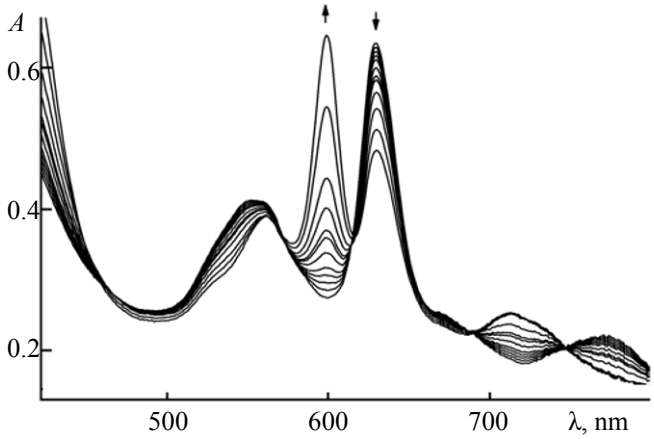


Fig. 2. Spectrophotometric titration of **I** (C_{porph} = 6.30×10^{-4} M) in the system DMSO–K[222]OH at the (K[222])OH concentration from 0 to 3.84×10^{-4} M.

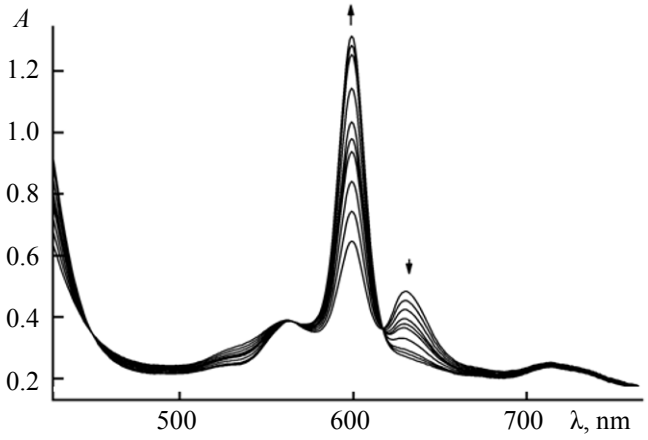


Fig. 3. Spectrophotometric titration of **I** (C_{porph} = 6.30×10^{-4} M) in the system DMSO–K[222]OH at the (K[222])OH concentration from 3.84×10^{-4} to 1.60×10^{-3} M.

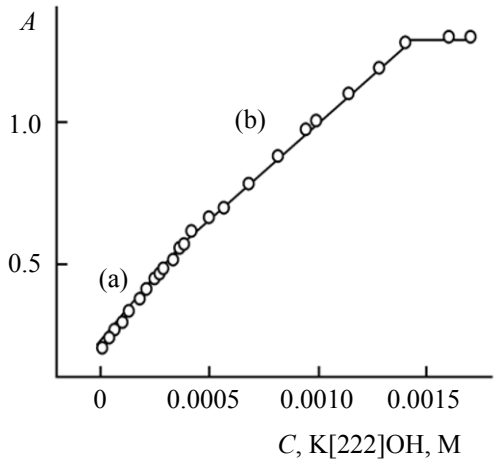


Fig. 4. Titration curve of **I** (C_{porph} = 6.30×10^{-4} M) in the system DMSO–K[222]OH at the analytical wavelength λ = 599 nm: (a) Step 1, the formation of HP^{-} (concentration of (K[222])OH from 0 to 3.84×10^{-4} M); (b) Step 2, the formation of P^{2-} (concentration of (K [222]) OH 3.84×10^{-4} to 1.60×10^{-3} M).

determining the constants was calculated as the arithmetic mean value of the constants in three parallel experiments; it amounted to 5–7%.

Upon titration of H_2BP in the system DMSO–K[222]OH (Fig. 5), in the EAS the successive formation of HP^{-} and P^{2-} forms was also observed. The titration curve has two sections, to each part its own family of spectral curves and the family of isosbestic points in the EAS corresponds. At the increase in pH of the solutions, in the reaction system with the participation of **II** the intensity and the blue shift of the absorption bands (~14 nm) significantly increased. Having determined the coordinates of the point of inflection of the titration curve (Fig. 5), the deprotonation processes in the system DMSO–K[222]OH were separated according to the sections and the corresponding constants by the formula (3) were calculated (Table 2).

Comparing the above results of spectrophotometric titration for the di- and triazaporphyrins it is seen that the number of *meso*-nitrogen atoms in the compound

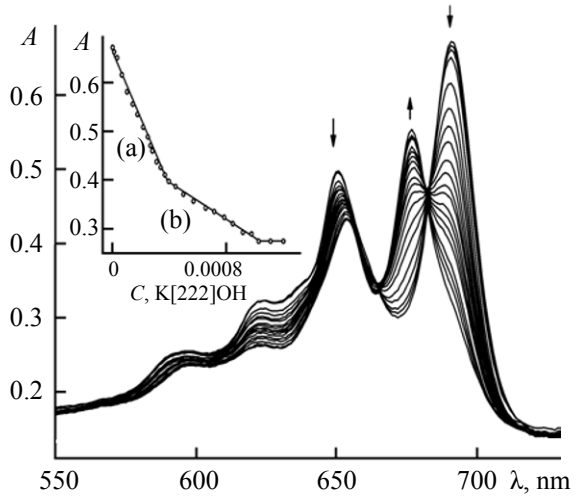


Fig. 5. Spectrophotometric titration of **II** (C_{porph} = 4.30×10^{-4} M) in the system DMSO–K[222]OH at the (K[222])OH concentration from 0 to 1.11×10^{-3} M, and the titration curve of compounds at the analytical wavelength λ = 691nm: (a) Step 1, the formation of HP^- (K[222])OH from 0 to 3.81×10^{-4} M); (b) Step 2, the formation of P^{2-} (K[222])OH from 3.81×10^{-4} to 1.11×10^{-3} M).

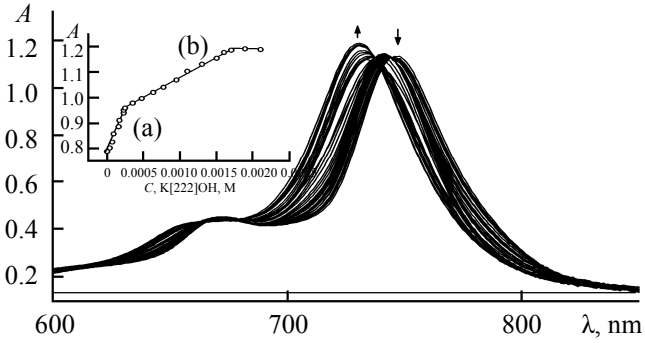


Fig. 6. Spectrophotometric titration **III** (C_{porph} = 5.5×10^{-4} M) in the system DMSO–K[222]OH at the (K[222])OH concentration from 0 to 1.88×10^{-3} M, and the titration curve for the compound at the analytical wavelength λ = 731 nm: (a) Step 1, the formation of HP^- (K[222])OH from 0 to 2.48×10^{-4} M), (b) Step 2, the formation of P^{2-} (K[222])OH from 2.48×10^{-4} to 1.88×10^{-3} M).

affects the acid properties of porphyrins in DMSO: An increase in the number of *meso*-nitrogen atoms increases the acidity of the compound, and the cleavage of the second proton from endocyclic nitrogen atom (Table 2) is easier than of the first. Changes in the EAS of compounds **I** and **II** show that the response of the system to the change in the environment pH is greater in the case of diaza-compounds.

Upon titration of $H_2PC(OAm)_8$, in the system DMSO–K[222]OH (Fig. 6), in the EAS the successive formation of HP^- and P^{2-} forms is also observed. The corresponding titration curve consists of two sections, each corresponding to its family of spectral curves in the EAS. Having determined the coordinates of the point of inflection on the titration curve (Fig. 6), the process of deprotonation of **III** in the system DMSO–K[222]OH was separated into steps and the corresponding constants were calculated along the formula (3) (Table 2). It should be noted that changes in the EAS with increase in pH in the case of compound **III**, as compared with **I** and **II**, are minimal, while the acid dissociation constants for **III** are the greatest.

Analyzing the numerical values of acid dissociation constants (Table 2), we can construct a series of acidity of the compounds corresponding to an increase in acid dissociation constants: **III** > **II** > **I**. For all three compounds, the dissociation in the second step is about 7 times easier than in the first. In addition, each step of deprotonation is accompanied by a strong response in

Table 1. Parameters of electron absorption spectra of some forms of compounds **I**, **II** and **III** (C_{porph} ~ 5.3×10^{-5} M) in DMSO in the presence of (K[222])OH (from 0 to 2×10^{-3} M)

Comp. no.	Compound	λ_1, nm (log ε)	λ_2, nm (log ε)	λ_3, nm (log ε)
I	H_2P	552 (2.81)	630 (3.02)	771 (2.54)
	HP^-	562 (2.79)	599 (3.01)	630 (2.88)
	P^{2-}	401 (3.32)	599 (3.33)	713 (2.57)
II	H_2P	651 (3.06)	–	691 (3.20)
	HP^-	653 (3.03)	–	675 (3.09)
	P^{2-}	655 (3.00)	–	677 (3.10)
III	H_2P	422 (3.01)	674 (2.94)	748 (3.34)
	HP^-	422 (3.03)	671 (2.93)	742 (3.34)
	P^{2-}	418 (3.09)	–	731 (3.36)

Table 2. Dissociation constants of compounds **I**, **II**, and **III** in the system DMSO–(K[222])OH at 298 K

Comp. no.	k_{a1}	k_{a2}
I	1.24×10^{-4}	8.61×10^{-4}
II	1.45×10^{-4}	9.55×10^{-4}
III	1.51×10^{-4}	9.85×10^{-4}

the visible absorption spectrum, namely, there is an opportunity to "manage" the physical and chemical properties of tetrapyrrole chromophore by changing the medium basicity. These results indicate that the investigated substituted azaporphyrins are promising basic compounds for the creation of pH-switchable molecular devices for the detection of cations in solution.

EXPERIMENTAL

Porphyrins **I** and **II** were synthesized and identified along the methods [10, 11], compound **III** was synthesized by the methods [8, 12]. Dimethyl sulfoxide (DMSO) from Aldrich containing less than 0.01% of water was not purified additionally. A solution of potassium cryptate in DMSO (K[222]OH) was obtained from potassium hydroxide and cryptand [222]. The spectrophotometric titration method has been described in detail in [8, 9].

ACKNOWLEDGMENTS

This work was supported by Russian Foundation for Basic Research (grants no. 09-03-00040-A and 09-03-97500-r_center_a) and the Programme no. 1 "Theoretical and experimental study of the nature of chemical bonding and mechanisms of the most important chemical reactions and processes," Russian Academy of Sciences.

REFERENCES

1. Ershov, Yu.V., *Kinetika i termodinamika biokhimicheskikh i fiziologicheskikh protsessov* (Kinetics and Thermodynamics of Biochemical and Physiological Processes), Moscow: Meditsina, 1990.
2. Buchachenko, A.L. and Vasserman, A.M., *Stabil'nye radikaly. Elektronnoe stroenie, reaktsionnaya sposobnost' i primenenie* (Stable Radicals. Electronic Structure and Application), Moscow: Khimiya, 1973.
3. Mironov, A.F., *Ros. Khim. Zh.*, 1998, vol. 42, p. 23.
4. Izmailov, N.A., *Elektrokhimiya rastvorov* (Electrochemistry of Solutions), Moscow: Khimiya. 1976.
5. *Problemy khimii rastvorov. Rastvory neelektrolitov v zhidkostyakh. Sbornik* (Problems of the Chemistry of Solutions. Solutions of Non-Electrolytes in Fluids. Collection), Krestov, G.A., Ed., Moscow: Nauka, 1989.
6. Berezin, B.D., *Koordinatsionnye soedineniya porphirinov i ftalotsianina* (Coordination Compounds of Porphyrin and Phthalocyanine), Moscow: Nauka, 1978.
7. Ivanova, Yu.B., Sheinin, V.B., Berezin, B.D., Simonova, O.R., and Chizhova, N.V., *Zh. Obshch. Khim*., 2001, vol. 71, no. 6, p. 916.
8. Donzello, M.P., Ercolani, C., Gaberkorn, A.A., Kudrik, E.V. Meneghetti, M., Marcolongo, G., Rizzoli, C., and Stuzhin, P.A., *Chem. Eur. J*., 2003, vol. 9, no. 17, p. 4009.
9. Ivanova, Yu.B., Churakhina, Yu.I., and Mamardashvili, N.Zh., *Zh. Obshch. Khim*., 2008, vol. 78, no. 4, p. 691.
10. Ivanova, Yu.B., Churakhina, Yu.I, Semeikin, A.S., and Mamardashvili, N.Zh., *Zh. Obshch. Khim*., 2009, vol. 79, no. 4, p. 670.
11. Ivanova, Yu.B., Churakhina, Yu.I., Semeikina, A.S., Kumeeva, R.S., and Mamardashvili, N.Zh., *Zh. Obshch. Khim.,* 2008, vol. 78, no. 10, p. 1972.
12. Stuzhin, P.A., *J. Porphyrins Phthalocyanines*, 2003, vol. 7, nos. 11, 12, p. 813.