Russian Journal of General Chemistry, Vol. 72, No. 7, 2002, pp. 1128–1131. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 7, 2002, pp. 1207–1210.
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A Spectropotentiometric Study of Association Equilibria of Cationic Acids of Mesoporphyrin IX Dimethyl Ester with Iodide Ions in Acetonitrile

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Received July 1, 2000

Abstract—The association equilibrium of porphyrinium ions of mesoporphyrin IX dimethyl ester (H_2MP) with iodide ions in acetonitrile was studied by spectropotentiometric titration. Two associates were revealed: $(H_4MP^{2+})(I^-)$ and $(H_4MP^{2+})(I^-)_2$; the electronic absorption spectra of these species were measured, and their formation constants were determined.

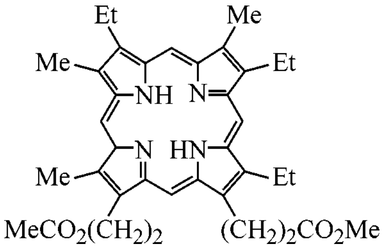
The acid–base properties of porphyrins are of large interest. The specific feature of porphyrins as multicentered bases is that the base centers (tertiary nitrogen atoms) are involved in a readily polarizable macrocyclic π system. On protonation, the positive charge becomes delocalized, causing appearance of fractional charges (δ^+) on all the atoms of the coordination core (N_4C_{12}) of porphyrins. Such delocalization of the positive charge in porphyrin cations determines certain specific features of their ion–ion interaction with acid anions, affecting the reactivity of porphyrins in acid solutions, their extraction from solution, and crystallization from solutions in organic solvents.

The coordination cavity of porphyrins contains two aza atoms capable of protonation in acid solutions with the formation of porphyrinium cations:

$$H_2P + H^+ \overset{K_1}{\rightleftarrows} H_3P^+, \quad (1)$$

$$H_3P^+ + H^+ \overset{K_2}{\rightleftarrows} H_4P^{2+}. \quad (2)$$

The H_4P^{2+} cations can coordinate counterions to form ion–ion associates [1]. Porphyrin salts $(H_4P^{2+})(X^-)_2$ ($X^- = I_3^-, I^-, Br^-, Cl^-, F^-, CF_3COO^-$) were isolated in the crystalline state and characterized by IR [1–4] and NMR [2] spectroscopy, and also by single crystal X-ray diffraction [4]. Compounds $(H_3P^+)X^-$ are studied poorly. The octaethylporphine derivative $(H_3OEP^+)(I_3^-)$ was isolated from chloroform and characterized by IR and electronic absorption (in $CHCl_3$ and MeOH) spectra [2]. Attempts [3] to isolate free monocationic derivative of blood porphyrins from methanol solutions failed.



H_2MP

Here we report on a quantitative study of association of porphyrinium ions of mesoporphyrin IX dimethyl ester (a structural analog of H_2OEP) with I^- ions in the system $MeCN–HClO_4–NaI$. Titration of H_2MP with perchloric acid is accompanied by two successive changes in the electronic absorption spectra (Fig. 1); each of these changes is characterized by an own set of isobestic points and a separate step in the titration curve (Fig. 2). The parameters of the electronic absorption spectra of H_2MP, H_3MP^+, and H_4MP^{2+} in acetonitrile are listed in the table.

The step protonation constants of mesoporphyrin IX dimethyl ether [reactions (1), (2)] were calculated with Eq. (3) by nonlinear least-squares fitting [5]: $\log K_1 = 11.95 \pm 0.03$ and $\log K_2 = 7.55 \pm 0.03$.

$$A_{550} = \frac{A_{H_2P} K_1 K_2 + A_{H_3P^+} a K_2 + A_{H_4P^{2+}} a^2}{K_1 K_2 + a K_2 + a^2}. \quad (3)$$

Here, A_{550} is the current optical density at 550 nm (analytical wavelength); A_{H_2P}, $A_{H_3P^+}$, and $A_{H_4P^{2+}}$ are the optical densities of solutions containing pure associates H_2MP, H_3MP^+, and H_4MP^{2+} (1.9×10^{-5} M); $a = 10^{-pH}$.

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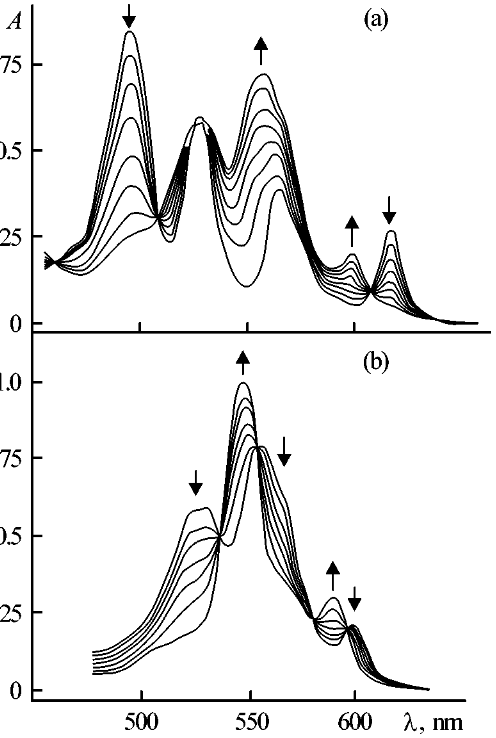

Fig. 1. Variation of the electronic absorption spectra of H_2MP in acetonitrile: (a) first (pH 10–16) and (b) second (pH 5–10) protonation steps (298 K).

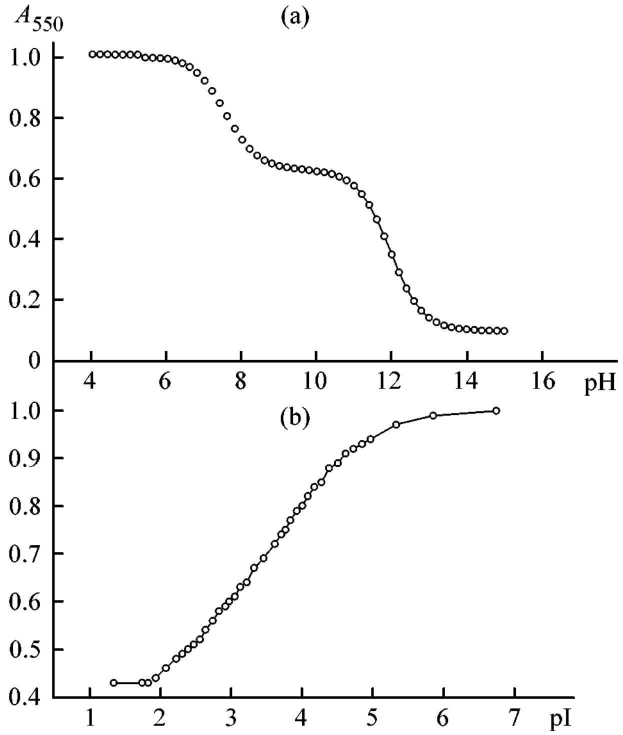

Fig. 2. Titration curves in acetonitrile (298 K) of (a) H_2MP with perchloric acid and (b) H_4MP^{2+} with NaI.

In the titration curve, we can distinguish three pH ranges practically corresponding to existence of individual species: H_2MP, pH > 13.5; H_3MP^+, pH 9.5–10.5; and H_4MP^{2+}, pH < 6.5. Owing to this fact, it appeared feasible to directly titrate the porphyrinium ions with an iodide solution. As the titrant we chose a solution of NaI in acetonitrile, because NaI is characterized by relatively low association constant in this solvent (K_{as} 10.0 [6]) as compared to other iodides.

The absence of HI associates in the ranges pH 5–15, pI 2–7 (288–318 K) was proved by additional potentiometric studies with a Crytur pI 53–27 ion-selective electrode in a standard spectropotentiometric cell [7].

The cations H_3MP^+ and H_4MP^{2+} were titrated at fixed pH (9.96 and 5.30, respectively), adjusted by microdosing of a perchloric acid solution. The analytical concentrations of reactants in each point were corrected for dilution of the working solution. The results of titrating H_4MP^{2+} are shown in Figs. 2 and 3.

With increasing concentration of iodide, the electronic absorption sectra of H_4MP^{2+} solutions underwent transformations with two sets of isobestic points: (1) 530 and 590 nm; (2) 535 and 595 nm. Such a pat-

Electronic absorption spectra of solutions of various porphyrin species in MeCN

Compound	λ_{max}, nm (log ε)				
H_2MP	497 (4.12)	531 (3.96)	568 (3.79)	621 (3.63)	
H_3MP^+	527 sh	532 (3.95)	558 (4.08)	569 sh	603 (3.51)
H_4MP^{2+}	510 sh	525 sh	550 (4.21)	570 sh	593 (3.71)
$(H_4MP^{2+})(I^-)_2$	562 (4.01)	582 sh			
$(H_3OEP^+)(I_3^-)$[a]		534 (3.95)	560 (4.08)	572 (3.98)	604 (3.58)
$(H_4OEP^{2+})(I_3^-)(I^-)$[a]	563 (3.98)	587 (3.70)	605 (3.56)		

[a] In $CHCl_3$.

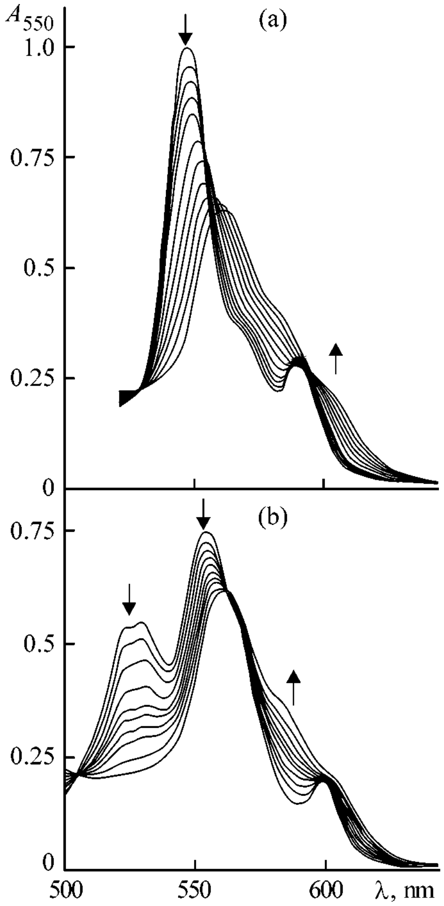

Fig. 3. Variation of the electronic absorption spectra in acetonitrile (298 K): (a) H_4MP^{2+}, pI 1.2–7, pH 5; (b) H_3MP^+, pI 1.5–3.5, pH 9.96.

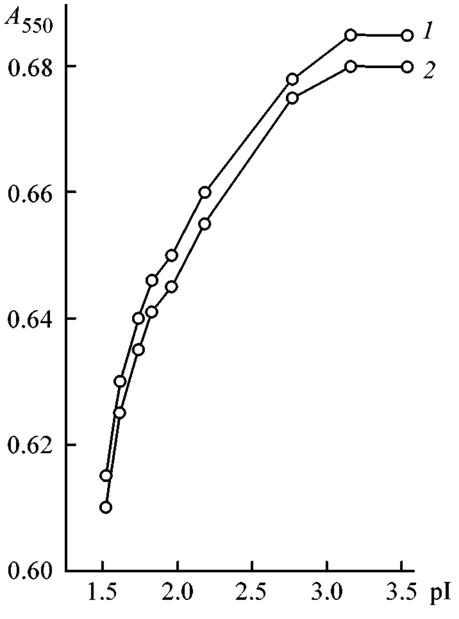

Fig. 4. Curves of H_3P^+ titration with an NaI solution at 298 K: (*1*) experimental and (*2*) calculated.

tern is due to successive formation of two kinds of iodide associates, with $H_4MP(I)_2$ as the final product (Fig. 3). The two successive processes give a common step in the titration curve, which is typical for processes whose constants differ by less than two orders of magnitude [5]. The constants of equilibria (4) and (5) were calculated by nonlinear least-squares fitting with Eq. (6): $\log K_I = 4.27 \pm 0.02$ and $\log K_{II} = 2.83 \pm 0.01$.

$$H_4MP^{2+} + I^- \overset{K_I}{\rightleftarrows} H_4MP(I)^+, \qquad (4)$$

$$H_4MP(I)^+ + I^- \overset{K_{II}}{\rightleftarrows} H_4MP(I)_2, \qquad (5)$$

$$A_{550} = \frac{A_{H_2P^{2+}} K_{II} K_I + A_{(H_4P^{2+})(I^-)}[I^-]K_I + A_{(H_4P^{2+})(I^-)_2}[I^-]^2}{K_{II}K_I + [I^-]K_{II} + [I^-]^2}. \qquad (6)$$

Here, $A_{H_4P^{2+}}$, $A_{(H_4P^{2+})I^-}$, and $A_{(H_4P^{2+})(I^-)^2}$ are the optical densities of 1.9×10^{-5} M solutions of the pure species H_4MP^{2+}, $(H_4MP^{2+})I^-$, and $(H_4MP^{2+})(I^-)^2$, respectively.

The sum of the equilibrium relative contents of H_2MP and H_3MP^+ at the start of titration did not exceed 0.6 mol % and was neglected in the calculations. The running values of $[I^-]$ in Eq. (6) were calculated from Eq. (7):

$$[NaI]_0 = K_{as}[I^-]^2 + [I^-], \qquad (7)$$

where $[NaI]_0$ is the initial analytical concentration of NaI.

Apparently, the structure of the associate $(H_4MP^{2+}) \cdot (I^-)_2$ is identical to that of porphyrin dihydrochlorides $(H_4P^{2+})(Cl^-)_2$ [1, 4, 8], in which two chloride anions are located axially on the opposite sides of the porphyrin macroring. As a result of interaction with the counterions in the associate $(H_4P^{2+})(X^-)_2$, the initially planar porphyrin ring becomes crimped [4]. Owing to mutual effect of the anions in $(H_4MP^{2+})(I^-)_2$, the constants K_{II} are lower than K_I. It is seen from the table that the electronic absorption spectrum of $(H_4MP^{2+})(I^-)_2$ and the spectrum assigned in [2] to $(H_4OEP^{2+})(I_3^-)(I^-)$ in CH_3Cl have similar parameters. However, we found no evidence of formation of a structure containing the I_3^- ion. The monohalide $(H_4MP^{2+})(I^-)$ was not detected previously. In titration of the H_3MP^+ ion, its electronic spectrum directly transforms into that of $(H_4MP^{2+})(I^-)_2$ with clear isobestic points at 504 and 570 nm (Fig. 3).

The results of calculation of the dependence $A_{550} = f(\text{pI, pH})$, performed without assuming formation of $(H_3MP^+)I^-$ [Eq. (8)], appeared to be nicely consistent with the experimental titration curve (Fig. 4).

$$A_{550} = \varepsilon_{H_2P}[H_2P] + \varepsilon_{H_3P^+}[H_3P^+] + \varepsilon_{H_4P^{2+}}[H_4P^{2+}]$$
$$+ \varepsilon_{(H_4P^{2+})I^-}[(H_4P^{2+})(I^-)] + \varepsilon_{(H_4P^{2+})(I^-)_2}[(H_4P^{2+})(I^-)_2]. \quad (8)$$

The single positive charge of H_3MP^+ may be insufficient to form associates with I^-. It is known that the $>$NH and $\geqslant$N groups of porphyrins are not solvated in solutions [9]. This fact is explained in [9] by intramolecular effects of atomic and π-electronic shielding of the coordination cavity of the macroring [10], which are also possible in planar H_3MP^+. A low stability of the associate $(H_3MP^+)I^-$ in solution may be an alternative explanation. The H_3MP^+ cation may be incapable of competing with the solvent for the nucleophilic species or may be considerably less stable than $(H_4MP^{2+})(I^-)_2$. This assumption is supported by theoretical calculations [8] of the thermodynamic stability of isolated associates of H_3P^+ with MeCN, H_2O, and Me_2SO. The electronic absorption spectra of solutions of H_3MP^+ in acetonitrile virtually coincide with those of solutions of $(H_3OEP^+)(I_3^-)$ in methanol and chloroform (see table), which may be due either to solvolysis of $(H_3OEP^+)(I_3^-)$ to H_3OEPP^+ or to the fact that the perturbation of the porphyrin aromatic system with the counterion is insignificant. Studies of transformations of H_2MP (a structural analog of H_2OEP) in the system $HClO_4$–NaI suggest that dissolution of the salt $(H_3OEP^+)(I_3^-)$ is accompanied by its complete dissociation.

EXPERIMENTAL

Mesoporphyrin IX dimethyl ester was prepared according to [11] and purified by chromatography (alumina, Brockmann grade II, eluent and solvent chloroform). The porphyrin purity was confirmed spectrophotometrically [12]. Sodium iodide (ultrapure grade) was dried in a vacuum (1.33 Pa) at 393 K for 2 days to constant weight. Acetonitrile (chemically pure grade) was purified by dynamic dehydration on a column packed with neutral alumina, which was followed by fractional distillation [13]. The residual moisture content in acetonitrile, determined by Fischer titration, did not exceed 0.01 wt %. The concentration of working solutions of H_2MP was 1.9×10^{-5} M in all the experiments.

The procedures for pretreatment of the other chemicals, the scheme of the cell, and the potentiometric titration procedure used to study the protonation equilibrium of H_2MP in acetonitrile are described in [7].

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