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Protonation of 5,10,15,20−Tetrakis(4−sulfonatophenyl)porphine in Water

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Protonation equilibriums of the porphyrin core H_2P in $H_2P(PhSO_3^-)_4$ with perchloric acid in water are investigated by methods of spectropotentiometry and computer chemistry (DFT/B3LYP and PM3). It is shown that leveling of step constants is caused by formation of aquacomplex $[H_4P^{2+}(PhSO_3^-)_4](H_2O)_2$ of diprotonated porphyrin platform showing properties of anion-molecular receptor. Values of K_1 (4.85 ± 0.03), $K_2{\cdot}K_3$(1.22 ± 0.03) are defined, and rough value of K_2 (-0.23) for reactions $H_2P + H^+ <=> H_3P^+$ (1); $H_3P^+ + H^+ <=> H_4P^{2+}$ (2); $H_4P^{2+} + 2H_2O <=> [H_4P^{2+}](H_2O)_2$ (3) is calculated. Molecular parameters $[H_4P^{2+}(PhSO_3^-)_4](H_2O)_2$ are calculated and it is established that receptor H_4P^{2+} possesses very high complementarity concerning two water molecules.

Keywords: 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphine, basicity, J-aggregates.

Introduction

Some porphyrins are perspective tectons for creation of supramolecular nanostructured materials on technology "from below upwards". Nanoscale porphyrin fibers, rods, ribbons, sheets, hollow hexagonal prisms, filled and hollow spheres, tubes, wheels and biomorphous crystals of the various form are received and actively investigated by this time.[1] Their firm nature and unique properties provide access to a new class of nanomaterials with potential possibilities of use in such important areas, as solar elements, photocatalysis, hydrogen power, electronics, nonlinear optics and chemosensors.

One of the perspective compounds is water-soluble 5,10,15,20-tetrakis(4-sulfophenyl)porphine $H_2P(PhSO_3H)_4$.

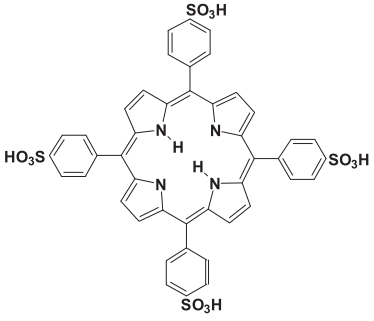
Molecule of $H_2P(PhSO_3H)_4$ consists of hydrophobic porphyrin platform-chromophore H_2P, and four peripheral hydrophilic sulfophenyl substituents -$PhSO_3H$, the combination of which provides its unique properties.

Zwitterion $H_4P^{2+}(PhSO_3^-)_4$ is tecton for p*H*-operated ionic self-assemble of supramolecular polymers $\{H_4P^{2+}(PhSO_3^-)_4\}_n$, named J-aggregates (in honor of Edvin Jelley[2]), organized as a bricklaying[3,4] which is formed as a result of interaction of phenylsulfonate groups -$PhSO_3^-$ ("tail") with diprotonated porphyrin platform H_4P^{2+} ("head"), showing properties of anion-molecular receptor.[5] In acidic water solution J-aggregates $\{H_4P^{2+}(PhSO_3^-)_4\}_n$ form solid one-wall tubes in diameter about 25 nanometers and length to 1 micron,[6] which drop out in a deposit. As formation of J-aggregates is kinetically hindered, it is possible to study the protonation equilibriums of porphyrin platform $H_2P(PhSO_3^-)_4$. Protolytic transformations of $H_2P(PhSO_3H)_4$ depending on p*H* of water solution are shown in Scheme 1.[4,7,8]

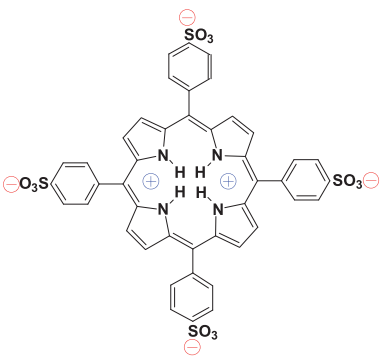
$$H_2P(PhSO_3^-)_4 \underset{}{\overset{pH\ 4.8}{\rightleftharpoons}} H_4P^{2+}(PhSO_3^-)_4 \overset{pH\ 2.6}{\rightleftharpoons}$$
$$\overset{pH\ 2.6}{\rightleftharpoons} H_4P^{2+}(PhSO_3^-)_2(PhSO_3H)_2 \overset{pH\ 1.1}{\rightleftharpoons} H_4P^{2+}(PhSO_3H)_4$$

Scheme 1. Transformations of $H_2P(PhSO_3H)_4$ depending on p*H* of water.

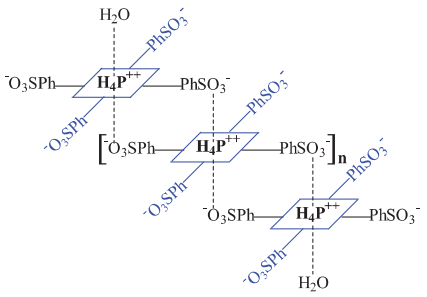
Published data testify that protonation equilibriums of $H_2P(PhSO_3^-)_4$ in a water solution have close values of step



$H_2P(PhSO_3H)_4$



$H_4P^{2+}(PhSO_3^-)_4$
zwitterion-tecton



J-aggregate (n >100000)

constants which have not been measured till now, and the reason of their leveling is not found out. For completion of this blank the study of protonation reactions of $H_2P(PhSO_3^-)_4$ in water was carried out by spectropotentiometric method and by methods of computer chemistry (DFT/B3LYP and PM3) in a hypothetical ideal gas phase.

Experimental

Synthesis. The tetraammonium salt of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphine was prepared according to the known procedure.[9]

Spectropotentiometry. The investigation of basicity of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphine was carried out by the spectropotentiometric method in system (I) at 298 K, as it was described earlier.[10] Electronic absorption spectra were obtained in water using AvaSpec-2048-2 for UV-visible spectroscopy.

$$H_2P(PhSO_3NH_4)_4 - HClO_4 - H_2O \qquad (I)$$

Calculation methods. Basicity constants of $H_2P(PhSO_3^-)_4$ were calculated by the method of fitting parameters using program SigmaPlot® software provided by Systat Software Inc. (SSI). Geometry optimizing calculations were carried out using DFT/B3LYP method with 3-21G** basis set. All calculations were performed with the Gaussian 98 program suite.[11]

Results and Discussion

Aquacomplex $[H_4P^{2+}(PhSO_3^-)_4](H_2O)_2$

Earlier, it has been shown that diprotonated porphyrin platform, showing properties of anion-molecular receptor-chromophore, forms steady complexes $[H_4P^{2+}](AN)_2$, $[H_4P^{2+}](AN)(H_2O)$, $[H_4P^{2+}](H_2O)_2$, $[H_4P^{2+}](AN)(Hal^-)$ and $[H_4P^{2+}](Hal^-)_2$. Formation constants of these complexes have been measured by spectropotentiometric method in acetonitrile (AN).[5,8,12,13] Geometry of anion-molecular complexes H_4P^{2+} and also enthalpy of guest linkages were studied by methods of computer chemistry DFT/B3LYP/3-21G**, PM3 and MMX.[5,13,14]

Results of DFT calculations of aquacomplex geometry $[H_4P^{2+}(PhSO_3^-)_4](H_2O)_2$ are shown in Figure 1.

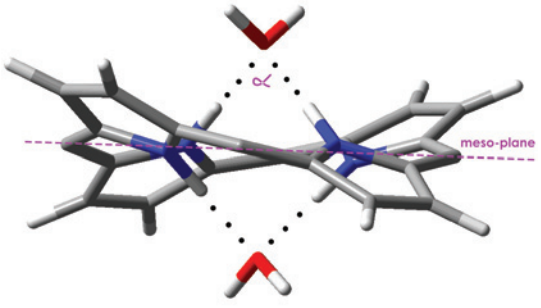


Figure 1. Geometry of solvatocomplex $[H_4P^{2+}(PhSO_3^-)_4](H_2O)_2$ (phenyl rings are not shown).

Initial diprotonated platform in structure of $H_4P^{2+}(PhSO_3^-)_4$ represents a symmetric 1,3-alternate with capture angles[15] α = 94° in each site of linkage. Each molecule of water is coupled by two hydrogen bonds with atoms of opposite NH-groups in such manner that their projections to 1.3-alternate mesoplane form angle of 90°. Elastic 1,3-alternate adapts to 2 molecules of water therefore the initial capture angle increases to 102°. In structure of aquacomplex, receptor $H_4P^{2+}(PhSO_3^-)_4$ gets almost ideal geometrical complementarity concerning two oxygen atoms, which is estimated by angles of hydrogen bonds N-H···O[5] of 178° (180° at ideal complementarity). Distance between the mesoplane of 1,3-alternate and oxygen atoms amounts 1.93 Å. Charge transfer (Mulliken charge) from oxygen atom on H_4P^{2+} makes about 20 %, and enthalpy of each molecule of water is 6.5 kcal/mole.

Protonation of $H_2P(PhSO_3^-)_4$ in Water

The diprotonated platform of zwitterion in water solution is in a kind of aquacomplex $[H_4P^{2+}(PhSO_3^-)_4](H_2O)_2$ (Figure 1) that it is necessary to consider at interpretation of spectropotentiometric experiment results. To exclude possibility of anionic complexes formation chloric acid was used in the work, since its anion is indifferent to H_4P^{2+}.[10]

Changes of an UV-vis spectrum of $H_2P(PhSO_3^-)_4$ at pH = 2-8 (Figure 2) are in equilibrium and pH-reversible. Full reversibility of spectral changes has been checked up specially in system $H_2P(PhSO_3NH_4)_4$ - $HClO_4$/KOH - H_2O. Time of achievement of equilibrium in experimental conditions is extremely fast and is limited only by rate of solution hashing.

With increase in acidity of solution the UV-vis spectrum of $H_2P(PhSO_3^-)_4$ is consequentially transformed into that of $H_3P^+(PhSO_3^-)_4$ and $[H_4P^{2+}(PhSO_3^-)_4](H_2O)$,[3,16] and the corresponding one-stage spectropotentiometric curves are observed (Figure 3).

In extreme range of acidity (4.3> pH> 5.3) in the UV-vis spectrum of system (I) two families of isosbestic points (421, 474, 560 nm and 425, 495 and 619 nm) are observed. The corresponding linear sections of the correlation dependence of optical density *vs* different absorption maxima are shown in Figure 4. These facts indicate coupled equilibria (1) and (2) between two pairs of light-absorbing centers H_2P/H_3P^+ and H_3P^+/H_4P^{2+} with close values of K_1 и K_2^*.[17]

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

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

$$H_4P^{++} + 2H_2O \overset{K_3}{\rightleftarrows} [H_4P^{++}](H_2O)_2 \qquad (3)$$

$$H_3P^+ + H^+ + 2H_2O \overset{K_2 \cdot K_3}{\rightleftarrows} [H_4P^{++}](H_2O)_2 \qquad (2, 3)$$

$$H_3P^+ + H^+ \overset{K_2^*}{\rightleftarrows} [H_4P^{++}](H_2O)_2 \qquad (4)$$

Calculation of K_1 and $K_2 \cdot K_3$ was performed by selecting the parameters in the equation (5) which connects pH value and current optical density A_T of solution at the analytical wavelength λ.[17]

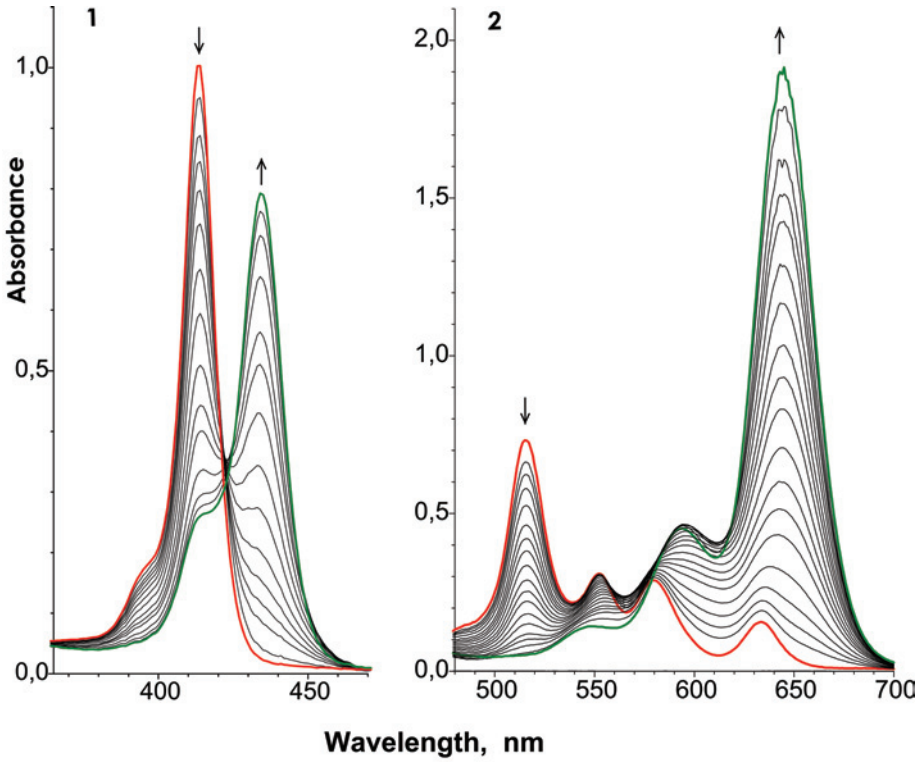


Figure 2. UV-vis spectra of system (I) at pH = 2-8, at porphyrin concentration $2.07\cdot10^{-5}$ mol/l (1) and $1.23\cdot10^{-4}$ mol/l (2): ↓ $H_2P(PhSO_3^-)_4$, ↑ $[H_4P^{2+}(PhSO_3^-)_4](H_2O)_2$.

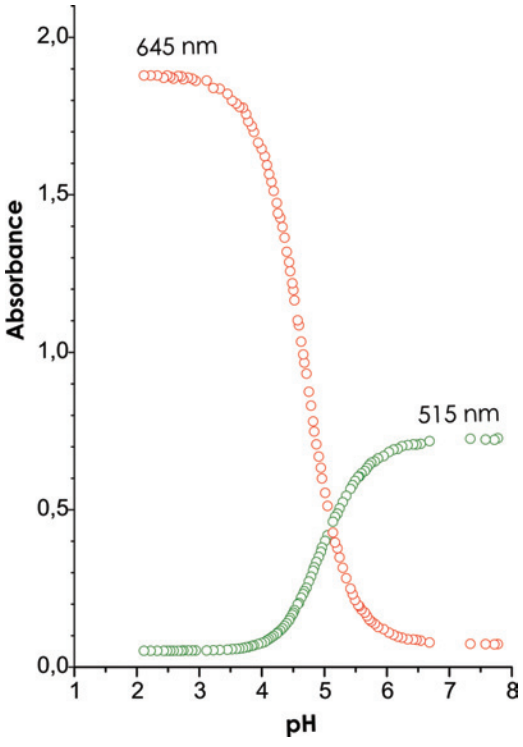


Figure 3. Spectropotentiometric curves in system (I).

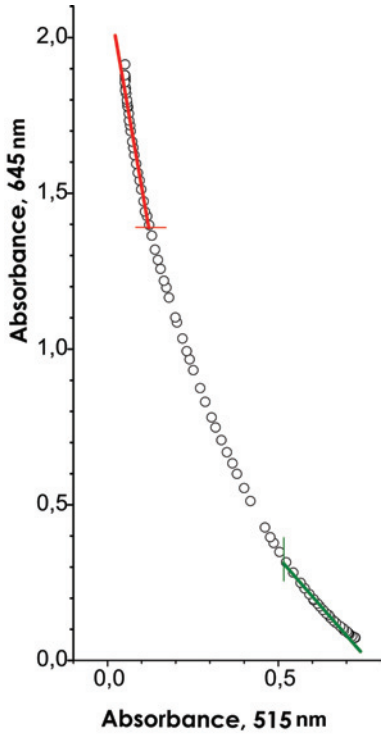


Figure 4. Correlation dependence of optical densities at 645 and 515 nm in system (I).

$$A_T^{\lambda} = \frac{(A^{o}_{H_2P} + A^{o}_{H_3P^+}\cdot K_1\cdot 10^{-pH} + A^{o}_{H_4P^{++}}\cdot K_1\cdot K_2\cdot K_3\cdot S^2\cdot 10^{-2pH})\cdot \ell}{1+K_1\cdot 10^{-pH} + K_1\cdot K_2\cdot K_3\cdot S^2\cdot 10^{-2pH}} \quad (5)$$

where $A^{o}_{H_2P}$, $A^{o}_{H_3P^+}$, $A^{o}_{H_4P^{++}(H_2O)_2}$ – optical densities of solution components at concentration equal to the analytical concentration of porphyrin C_o ($A^{o}_{i} = \varepsilon_i\cdot\ell\cdot C_o$), S - concentration of water in water at 298 K.

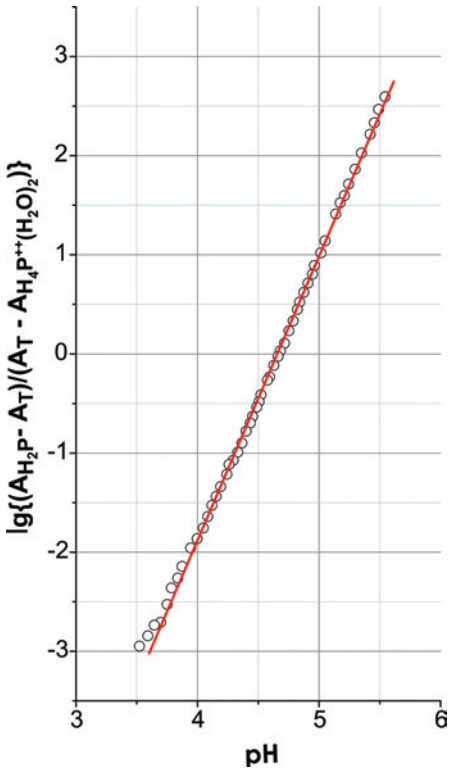


Figure 5. Dependence of lg(I_n) on p*H* for $H_2P(PhSO_3^-)_4$ in system (I).

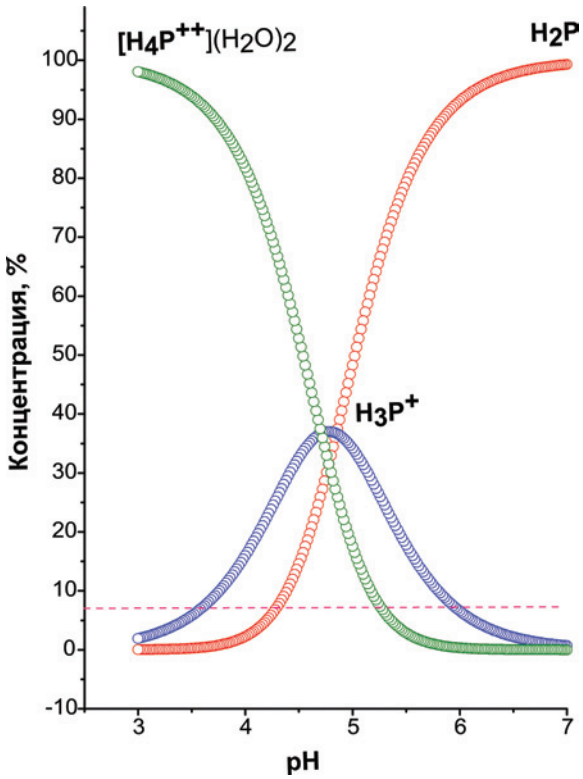


Figure 6. Distribution of equilibrium concentrations of H_2P, H_3P^+ and $[H_4P^{2+}](H_2O)_2$ in system (I).

Constants of $H_2P(PhSO_3^-)_4$ protonation in water were calculated on a titration curve at 645 nm (Figure 3). As a result of averaging of calculations on three independent experiments, values of lgK_1 = 4.85 ± 0.03 and $lg(K_2 \cdot K_3)$ = 1.22 ± 0.03 have been received. The correlation coefficient *R* of experimental and modeling dependences in all cases wasn't worse 0.9999. With a glance of work results[8] rough value of lgK_2 makes nearby -0.23 (lgK_3 = 1.45 for dimethyl ether of mesoporphyrin IX in AN at 298K), and full size of leveling effect in water nearby 4.94 (2lgS + lgK_3). Due to this circumstance, value of lgK_2^* (a conditional constant[18] of the second step of protonation) which is usually calculated from spectropotentiometric titration results of porphyrins on the equation (4), makes 4.71 ± 0.03, that is practically coincides with lgK_1. The experimental dependence (6) shown in Figure 5, is linear (*R* = 0.999) and characterized by high steepness (coefficient 2.82 *vs* 1 for one-proton reaction) that allows to use function p*H* as the effective switch of self-assemble of J-aggregates $\{H_4P^{2+}(PhSO_3^-)_4\}_n$.

$$\lg\left(\frac{A^{o}_{H_2P}-A_T}{A^{o}_{T}-A_{H_4P^{++}}}\right) = 2.82\times pH - 13.11;\ R=0.999 \qquad (6)$$

where A_T – current value of optical density on analytical wavelength of 645 nm.

For the description of the equilibrium mixture H_2P, H_3P^+ and $[H_4P^{2+}](H_2O)_2$ in system (I) the inverse problem was solved and the current values of component concentrations in range of p*H* 3-7 (Figure 6) were calculated. The Figure 6 shows that at experimental conditions a maximum value of H_3P^+ concentration reaches only 37 %. All UV-vis spectra in p*H* range are the superposition of three light-absorbing centers of H_2P, H_3P^+ and H_4P^{2+}, and isosbestic points are formed when concentration of one of three absorbing centers falls below 7 %.

Conclusions

Leveling of protonation step constants of $H_2P(PhSO_3^-)_4$ is caused by formation of aquacomplex $[H_4P^{2+}(PhSO_3^-)_4](H_2O)_2$ of diprotonated porphyrin platform showing properties of anion-molecular receptor.

The value of leveling effect is determined by multiplication of aquacomplex formation $[H_4P^{2+}(PhSO_3^-)_4](H_2O)_2$ constant and a square of concentration of water in water.

Diprotonated porphyrin platform of $H_4P^{2+}(PhSO_3^-)_4$ possesses very high complementarity concerning two water molecules.

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