

## Protonation Equilibriums of Porphin, 5,10,15,20–Tetraphenylporphin, 5,10,15,20–Tetrakis(4'–sulfonatophenyl)porphin in Methanol

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*The comparative investigation of substituent effects and media effects in relation to protonation equilibriums of porphyrinic platform ( $H_2P$ ) in series of porphin, 5,10,15,20-tetraphenylporphin and 5,10,15,20-tetrakis(4'-sulfonatophenyl)porphin was carried out by spectropotentiometric and computer chemistry (PM3) methods in methanol at 298 K. It was shown, that the receptor  $H_4P^{++}$  forms methanol solvatocomplexes  $[H_4P^{++}](CH_3OH)$  like "roost" and  $[H_4P^{++}](CH_3OH)_2$  like "double roost", but the equilibriums of the second protonation step of porphyrins practically are totally shifted to  $[H_4P^{++}](CH_3OH)_2$ . The appropriate step protonation and complexation constants were determined. It was determined, that media effects are the reason of the leveling of the step protonation constants of porphyrins, measured by spectrophotometric method, which "doesn't distinguish" the light-absorbing centers  $H_4P^{++}$ ,  $[H_4P^{++}](CH_3OH)$  and  $[H_4P^{++}](CH_3OH)_2$ .*

**Keywords:** Tetra(sulfonatophenyl)porphin, protonation, pH-controlled receptor, J-aggregates.

## Равновесия протонирования порфина, 5,10,15,20–тетрафенилпорфина и 5,10,15,20–тетракис–(4'–сульфонатофенил)порфина в метаноле

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*Методами спектропотенциометрии и компьютерной химии (PM3) выполнено сравнительное исследование эффектов заместителей и эффектов среды в отношении равновесий протонирования порфириновой платформы ( $H_2P$ ) в ряду порфин, 5,10,15,20-тетрафенилпорфин и 5,10,15,20-тетракис(4'-сульфонатофенил)порфин в метаноле при 298 К. Показано, что рецептор  $H_4P^{++}$  образует метанольные сольватоккомплексы  $[H_4P^{++}](CH_3OH)$  типа "наседст" и  $[H_4P^{++}](CH_3OH)_2$  типа "двойной наседст", но равновесия второй ступени протонирования практически полностью сдвинуты в сторону  $[H_4P^{++}](CH_3OH)_2$ . Определены соответствующие ступенчатые константы протонирования и комплексообразования. Установлено, что эффекты среды являются причиной нивелирования ступенчатых констант протонирования порфиринов, измеренных спектрофотометрическим методом, который "не различает" поглощающие центры  $H_4P^{++}$ ,  $[H_4P^{++}](CH_3OH)$  и  $[H_4P^{++}](CH_3OH)_2$ .*

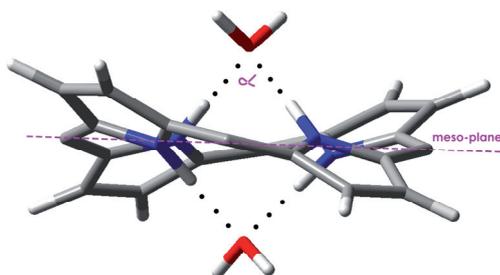
**Ключевые слова:** Тетра(сульфонатофенил)порфин, протонирование, pH-управляемый рецептор, J-агрегаты.

## Introduction

The formal equations, which are usually used for investigation of reaction of porphyrin protonation (1, 2) and other organic compounds, are equations of proton affinity and don't carry any information about medium effects.



Previously we have shown, that porphyrinic platform  $\text{H}_2\text{P}$  can be diprotonated forming  $\text{H}_4\text{P}^{++}$  receptor, which generates homogeneous 1:G:G and mixed 1:G<sub>1</sub>:G<sub>2</sub> complexes like “double roost” (Figure 1) type with solvents hydrogen bond acceptors and anions as guests.<sup>[1-5]</sup> The investigation of formation processes of solvatochemicals  $[\text{H}_4\text{P}^{++}]\text{S}$  and  $[\text{H}_4\text{P}^{++}]\text{S}_2$  is complicated by the absence of  $\text{H}_4\text{P}^{++}$  optical response. We suppose, that in ionizing solvent the second protonation always starts instantaneous self-assembly of solvatochemical  $[\text{H}_4\text{P}^{++}]\text{S}_2$ , which is the most stable particle in presence of indifferent acid anion (*e.g.* perchlorate or triflate).



**Figure 1.**  $[\text{H}_4\text{P}^{++}](\text{H}_2\text{O})_2$ <sup>[5]</sup>

These specific interactions, where the solvent plays the role of a reagent, influences on the result of  $\text{H}_2\text{P}$  protonation in the solvents of different composition. Previously we have shown, that formation of aquacomplex  $[\text{H}_4\text{P}^{++}(\text{PhSO}_3^-)](\text{H}_2\text{O})_2$  is one of the reasons for the synchronous diprotonation of this compound in water ( $\lg K_{b1}$  and  $\lg K_{b2}$  equal to 4.85 and 4.71, respectively).<sup>[5]</sup> But the role of the substituents and other medium effects were not determined. Significance of this investigations

is determined by the fact, that zwitterions  $\text{H}_4\text{P}^{++}(\text{PhSO}_3^-)_4$  are tectons for *pH*-controlled ionic self-assembly of porphyrinic *J*-aggregates and nanotubes on their basis, possessing interesting chemical, optical and electronic properties, which can be applied for developing the nanodevices.<sup>[6]</sup>

The aim of this study was the comparative investigation of substitution effects and solvent effects in relation to protonation equilibrium  $\text{H}_2\text{P}$  in series of porphin ( $\text{H}_2\text{Por}$ ), 5,10,15,20-tetraphenylporphin ( $\text{H}_2\text{PPh}_4$ ) and 5,10,15,20-tetrakis(4'-sulfonatophenyl)porphin in methanol. Methanol was chosen as the suitable solvent for this porphyrins and for potentiometry with glass *pH*-electrode.<sup>[7]</sup> Besides, *J*-aggregates self-assemble from  $[\text{H}_4\text{P}^{++}(\text{PhSO}_3^-)](\text{CH}_3\text{OH})_2$  sufficiently slowly in methanol, which allows to investigate the protonation equilibria of  $\text{H}_2\text{P}(\text{PhSO}_3^-)_4$  with no complications, just like in water.

## Experimental

**Synthesis.** Porphin ( $\text{H}_2\text{Por}$ ), 5,10,15,20-tetraphenylporphin ( $\text{H}_2\text{P}(\text{Ph})_4$ ) and 5,10,15,20-tetrakis(4'-sulfonatophenyl)porphin ( $\text{H}_2\text{P}(\text{PhSO}_3\text{H})_4$ ) in the form of tetrahydrate of tetraammonium salt were obtained by the well-known methods.<sup>[8-10]</sup>

**Spectropotentiometry.** The investigation of protonation equilibria of  $\text{H}_2\text{Por}$ ,  $\text{H}_2\text{P}(\text{Ph})_4$  and  $\text{H}_2\text{P}(\text{PhSO}_3^-)_4$  was carried out by spectropotentiometric method at 298 K.<sup>[1,5]</sup> We add, that we used spectropotentiometric cell in 100 ml volume with optical path length of 3.5 cm. The glass electrode was graduated in water buffer solutions by Equation 3 with a glance correction for proton activity coefficient in methanol.<sup>[7,11]</sup>

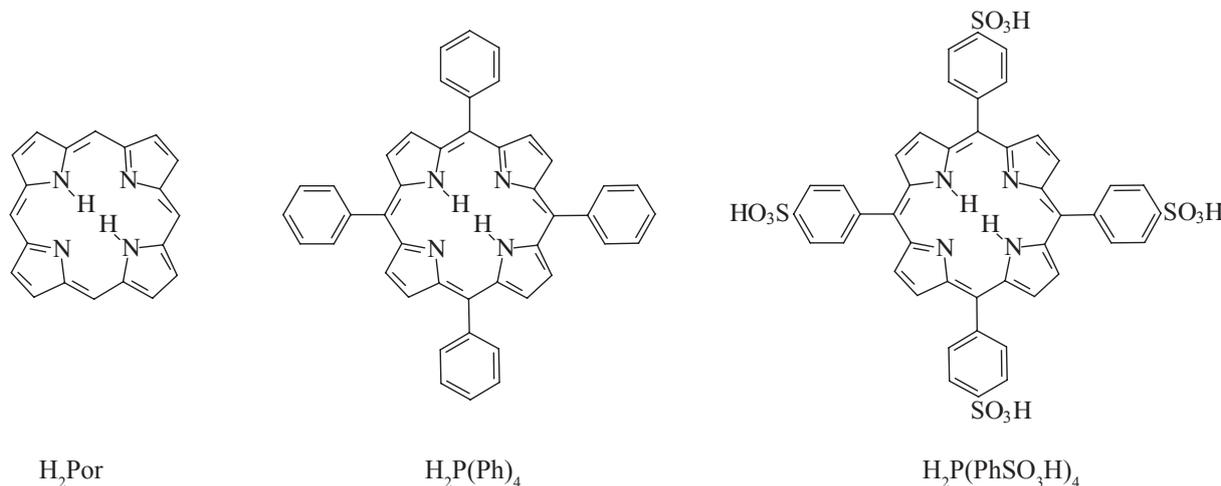
$$\text{pH}_{\text{MeOH}} = \text{pH}_{\text{H}_2\text{O}} + 2.34 \quad (3)$$

The electronic absorption spectra were recorded by spectrophotometer AvaSpec-2048-2 (180-1100 nm).

**Calculations.** The protonation constants  $K_{b1}$  and  $K_{b2}$  were calculated by the method of fitting parameters in Equation 4<sup>[12]</sup> using program SigmaPlot® software provided by Systat Software Inc. (SSI).

$$A_t = \frac{A_{0(\text{H}_2\text{P})} + K_{b1} \cdot 10^{-\text{pH}} \cdot A_{0(\text{H}_3\text{P}^+)} + K_{b2} \cdot 10^{-2\text{pH}} \cdot A_{0(\text{H}_4\text{P}^{++})}}{1 + K_{b1} \cdot 10^{-\text{pH}} + K_{b2} \cdot 10^{-2\text{pH}}} \quad (4)$$

Where  $A_t$  is the current value of solution absorbance on analytic wavelength;  $A_{0(\text{H}_2\text{P})}$ ,  $A_{0(\text{H}_3\text{P}^+)}$  and  $A_{0(\text{H}_4\text{P}^{++})}$  are the component absorbance, corresponding to the analytical porphyrin concentration ( $A^0 = C_{\text{H}_2\text{P}}^0 \cdot \varepsilon \cdot l$ ).



## Protonation Equilibria of Porphyrins in Methanol

The enthalpies of chemical reactions in the ideal hypothetical gas phase were calculated in terms of Hess law on the basis of PM3-formation enthalpies of reagents.

## Results and Discussion

### Porphyrin Protonation in Methanol

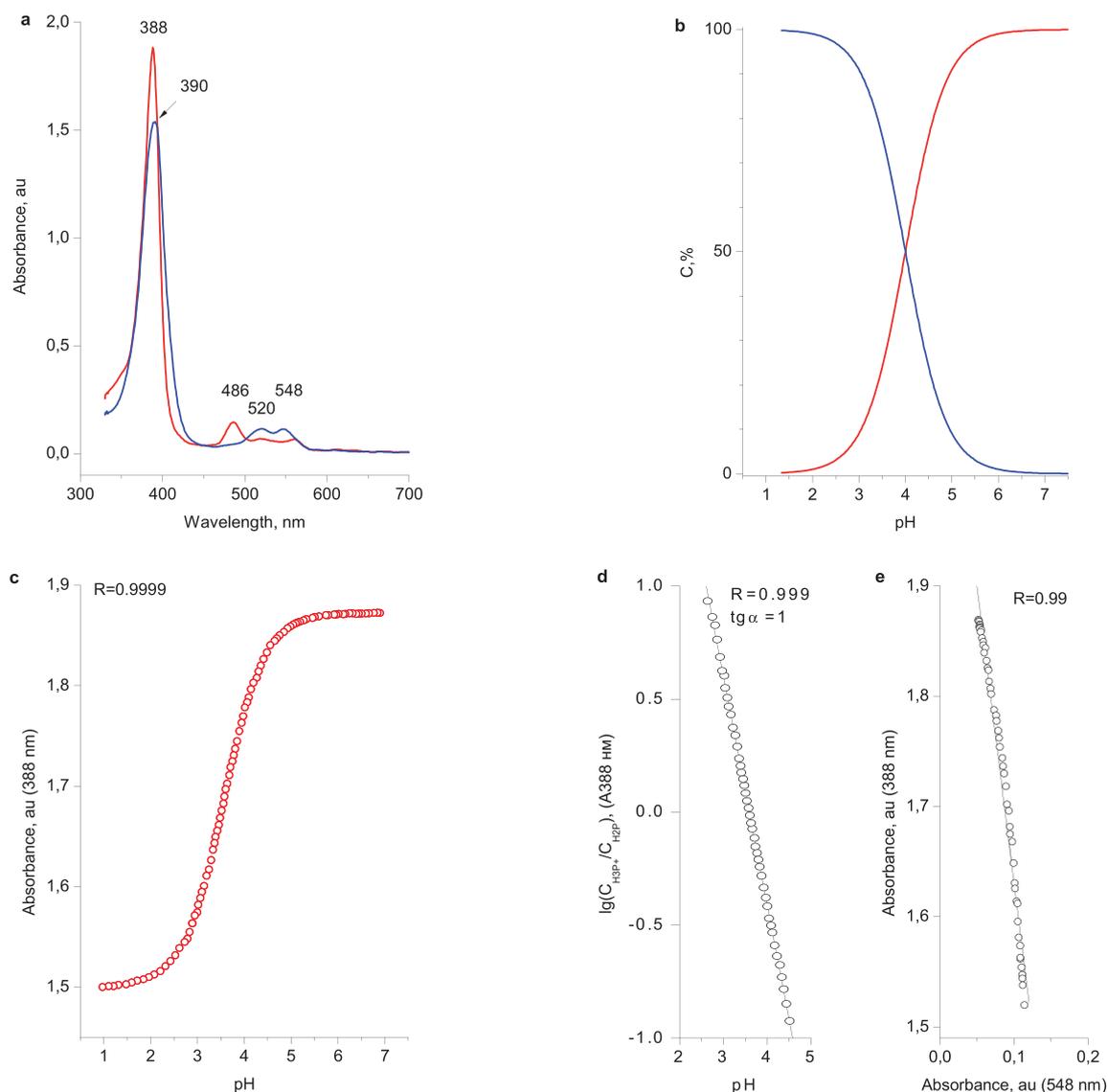
**H<sub>2</sub>Por.** In methanol, only one protolytic Equilibrium 1 between light-absorbing centers H<sub>2</sub>P and H<sub>3</sub>P<sup>+</sup> (Figure 2a,b) was found, which is confirmed by the single assemblage of isosbestic points at 362, 394, 447, 501 and 564 nm and by linear correlation between  $A^t$  of absorption bands in UV-Vis spectra (Figure 2e). The spectropotentiometric titration curve (Figure 2c) is single-step, and the relation  $\lg(C_{H_3P^+}/C_{H_2P}^0) = n \cdot pH - \lg K_{b1}$  (Figure 2d) is characterized by the constant of proportionality  $n$  (it determines the number of protons, added to H<sub>2</sub>Por) exactly equal to one. The  $\lg K_{b1}$  value for H<sub>2</sub>Por in methanol is  $3.59 \pm 0.03$  (Table 1).

**H<sub>2</sub>P(Ph)<sub>4</sub>.** Phenyl substituents increase the basicity of the porphyrinic platform and shift the titration curve of

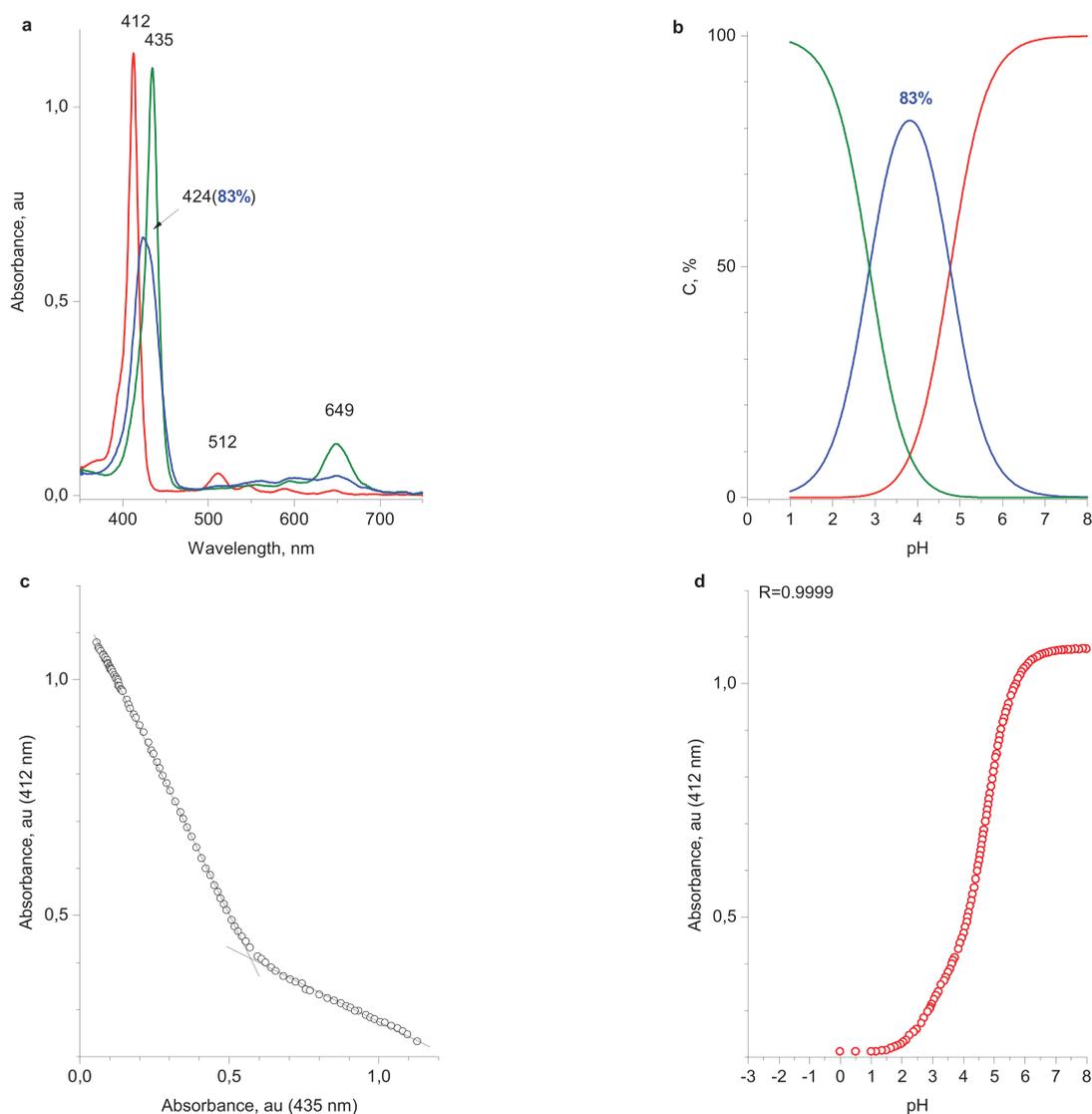
**Table 1.** Conditional protonation constants of porphyrins in methanol.

Porphyrin	$\lg K_{b1} \pm 0.03$	$\lg K_{b2} \pm 0.03$	$\lg K_{b2} - \lg K_{b1}$
H <sub>2</sub> Por	3.59		
H <sub>2</sub> P(Ph) <sub>4</sub>	4.77	2.87	-1.90
H <sub>2</sub> P(PhSO <sub>3</sub> <sup>-</sup> ) <sub>4</sub>	5.98	4.37	-1.61

H<sub>2</sub>P(Ph)<sub>4</sub> into the region of greater pH values (Figure 3d). Due to these facts, both protonation steps for H<sub>2</sub>P(Ph)<sub>4</sub> can be observed in methanol. The first (1) and the second (2) protonation steps correspond to their own families of isosbestic points at 419, 494 and 523 nm (H<sub>2</sub>P(Ph)<sub>4</sub><sup>+</sup>/H<sub>3</sub>P(Ph)<sub>4</sub><sup>+</sup>) and 367, 427, 447 and 621 nm (H<sub>3</sub>P(Ph)<sub>4</sub><sup>+</sup>/[H<sub>4</sub>P(Ph)<sub>4</sub><sup>++</sup>](CH<sub>3</sub>OH)<sub>2</sub>) respectively, and to the line sections of correlation dependence  $A^t_{412} = f(A^t_{435})$  (Figure 3c). The measured  $\lg K_{b1}$  and  $\lg K_{b2}$  \* values were  $4.77 \pm 0.03$  and  $2.87 \pm 0.03$ , respectively (Table 1). The titration curve is characterized by the small difference  $\lg K_{b2} - \lg K_{b1} = -1.90$ , therefore it is smooth, and the maximum of  $C_{H_3P(Ph)_4^+}$  is only 83% at pH 3.82 (Figure 3a,b).



**Figure 2.** Results of spectropotentiometric titration of H<sub>2</sub>Por by perchloric acid in methanol at 298 K: H<sub>2</sub>P (red), H<sub>3</sub>P<sup>+</sup> (blue).



**Figure 3.** Results of spectropotentiometric titration of  $\text{H}_2\text{P}(\text{Ph})_4$  by perchloric acid in methanol at 298 K:  $\text{H}_2\text{P}$  (red),  $\text{H}_3\text{P}^+$  (blue),  $[\text{H}_4\text{P}^{++}]$  ( $\text{CH}_3\text{OH}$ )<sub>2</sub> (green).

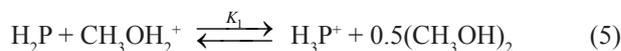
**$\text{H}_2\text{P}(\text{PhSO}_3^-)_4$ .** The protonation results of  $\text{H}_2\text{P}(\text{PhSO}_3^-)_4$  (Figure 4 a,c-e) and  $\text{H}_2\text{P}(\text{Ph})_4$  are similar, but sulfonate groups shift the titration curve into the region of greater pH values and decrease  $\lg K_{b2} - \lg K_{b1}$  from -1.90 down to -1.61 (Table 1). As a result, the maximum value of  $C_{\text{H}_3\text{P}^+}$  decreases to 77% (at  $\text{pH}=5.10$ ). The first and the second protonation steps correspond to their own families of isosbestic points at 421, 484, 527 nm and 374, 430, 452, 620 nm, and to the two line sections on correlation dependence  $A_{412}^t = f(A_{435}^t)$  (Figure 4c). Weak absorbance at 489 and 700 nm, which signalizes about the self-assembly of *J*-aggregates, appears only at the finish line of titration. We should note, that the more basic water eliminates  $K_{b1}$  and  $K_{b2}$  for  $\text{H}_2\text{P}(\text{PhSO}_3^-)_4$  more than methanol. The transfer of Reactions 1 and 2 from methanol to water decreases the value  $\lg K_{b2} - K_{b1}$  for  $\text{H}_2\text{P}(\text{PhSO}_3^-)_4$  down to 0.14. [5]

### Effects of Substituents and Media

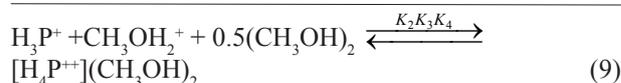
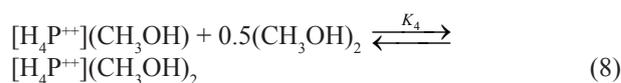
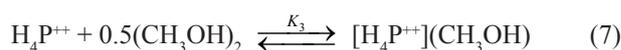
The Equilibriums of I and II protonation steps of  $\text{H}_2\text{P}$  in methanol can be characterized by Equations 5-8 with regarding specific interactions of solvent with  $\text{H}_4\text{P}^{++}$ ,  $\text{H}^+$  and its self-

association, where the solvent is a reagent, with generating of solvatocomplexes  $[\text{H}_4\text{P}^{++}]\text{CH}_3\text{OH}$ ,  $[\text{H}_4\text{P}^{++}](\text{CH}_3\text{OH})_2$ , solvated protons  $\text{CH}_3\text{OH}_2^+$  and dimers  $(\text{CH}_3\text{OH})_2$ . [13]

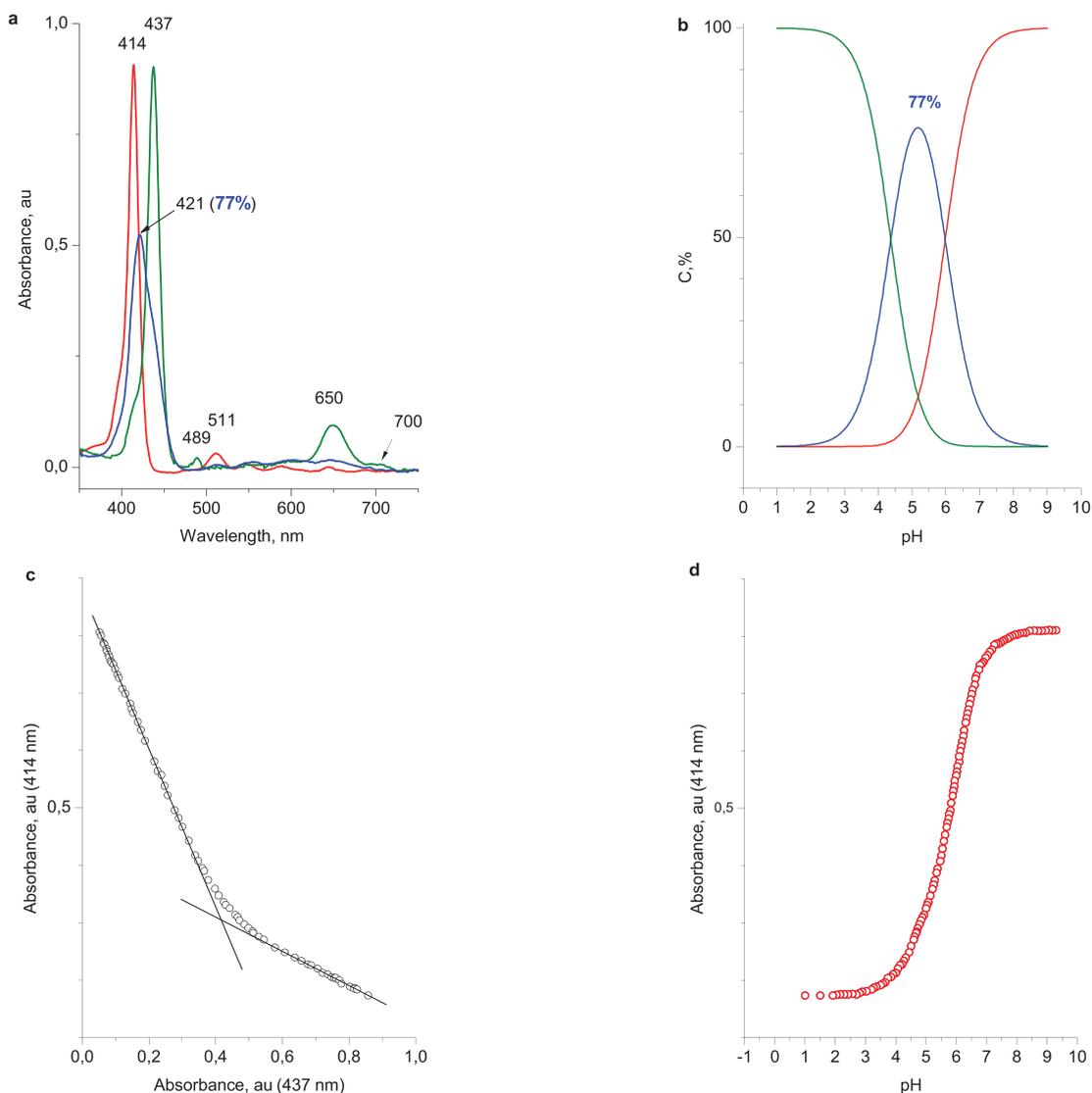
I protonation step



II protonation step



In this case,  $K_{b1}$  and  $K_{b2}$ , determined from the titration curve  $A_\lambda = f(\text{pH})$  by Equation 4, are conditional, [14] because  $K_{b1} = K_1/C_s$ ,  $K_{b2} = K_2 K_3 K_4 C_s$  (here  $C_s$  is the concentration



**Figure 4.** Results of spectropotentiometric titration of  $\text{H}_2\text{P}(\text{PhSO}_3^-)_4$  by perchloric acid in methanol at 298 K:  $\text{H}_2\text{P}$  (red),  $\text{H}_3\text{P}^+$  (blue),  $[\text{H}_4\text{P}^{++}](\text{CH}_3\text{OH})_2$  (green).

(activity) of solvent in solution). The value of  $K_3K_4C_s^2$  is the measure of leveling effect of a solvent in relation to conditional constants  $K_{b1}$  and  $K_{b2}$ . The  $K_2$ ,  $K_3$  and  $K_4$  values can be measured only in the form of  $K_2K_3K_4$ , and  $C_s$  can be calculated by the formula:  $C_s = 1000 \cdot \rho/M$ , which shows, that the leveling effect  $C_s^2$  of the certain solvent is determined by its density and molecular mass.

In order to differentiate the substituents' effects and media effects in protonation reactions of porphyrins, we used the Equations 10 and 11 at 298 K.

$$\Delta_s G^0 = \Delta_g G^0 - \Delta_{tr} G^0 \quad (10)$$

$$\Delta_s G^0 = -1.3639 \cdot \lg K \quad (11)$$

Where  $\Delta_s G^0$  and  $\Delta_g G^0$  are the standard Gibbs energies of chemical reaction in solution and in absence of media in hypothetical ideal gas phase, respectively, and  $\Delta_{tr} G^0$  is the Gibbs energy of chemical reaction transfer into solution,  $K$  is the thermodynamic equilibrium constant.

In this case,  $\Delta_g G^0$  is the measure of absolute (maximal) chemical affinity of the reagents, which depends only on

their molecular structure, and  $\Delta_{tr} G^0$  is the measure of media effects, that reduce  $\Delta_g G^0$ . For I and II protonation steps of  $\text{H}_2\text{P}$  in methanol, the expressions 10, 11 are transformed to 12 and 13, respectively.

$$\Delta_s G_I^0 = -(\text{PA}_{\text{H}_2\text{P}} - \text{PA}_{\text{CH}_3\text{OH}}) + 0.5 \Delta_g G^0_{(\text{CH}_3\text{OH})_2} - \Delta_{tr} G_I^0 \quad (12)$$

$$\Delta_s G_{II}^0 = -(\text{PA}_{\text{H}_3\text{P}^+} - \text{PA}_{\text{CH}_3\text{OH}}) + 0.5 \Delta_g G^0_{(\text{CH}_3\text{OH})_2} + \Delta_g G_3^0 + \Delta_g G_4^0 - \Delta_{tr} G_{II}^0 \quad (13)$$

Where  $\text{PA}_{\text{H}_2\text{P}}$ ,  $\text{PA}_{\text{H}_3\text{P}^+}$  and  $\text{PA}_{\text{CH}_3\text{OH}}$  make the proton affinity ( $\text{PA} = -\Delta_g G^0_{298\text{K}}$ ),  $\text{PA}_{\text{CH}_3\text{OH}}$ ,  $\Delta_g G^0_{(\text{CH}_3\text{OH})_2}$ ,  $\Delta_g G_3^0$  and  $\Delta_g G_4^0$  are contributions of specific interactions,  $\Delta_{tr} G_I^0$  and  $\Delta_{tr} G_{II}^0$  are the energies of reactions 5 and 9 transfer from gas phase into methanol.

### Internal Substituent Effects

The internal<sup>[10]</sup> (absolute) substituent effects in the absence of medium  $\delta_R \Delta_{\text{int}} G^0_{b1}$  and  $\delta_R \Delta_{\text{int}} G^0_{b2}$  can be calculated on the basis of  $\text{PA}_{\text{H}_2\text{P}}$  and  $\text{PA}_{\text{H}_3\text{P}^+}$ , which are the measure of maximal basicity of  $\text{H}_2\text{P}$  and  $\text{H}_3\text{P}^+$ , or on the basis of

**Table 2.** Internal substituent effects

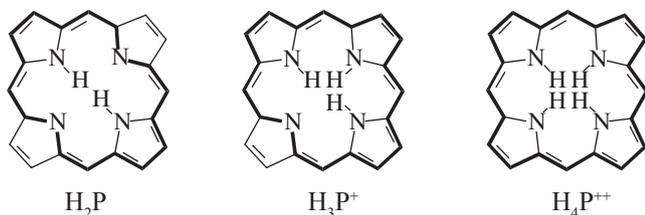
Basis	R	$\Delta_{\text{g}}H_{\text{b1}}^0$		$4\delta_{\text{R}}\Delta_{\text{int}}G_{\text{b1}}^0$		$\Delta_{\text{g}}H_{\text{b2}}^0$		$4\delta_{\text{R}}\Delta_{\text{int}}G_{\text{b2}}^0$	
		kcal/mol		%		kcal/mol		%	
H <sub>2</sub> Por		-209.62				-135.61			
H <sub>2</sub> P(Ph) <sub>4</sub>	-Ph	-213.99	-4.37	2.08%		-152.84	-17.23	12.71%	
H <sub>2</sub> P(PhSO <sub>3</sub> <sup>-</sup> ) <sub>4</sub>	-PhSO <sub>3</sub> <sup>-</sup>	-351.71	-142.09	67.78%		-295.83	-160.22	118.15%	

appropriate enthalpies of  $\Delta_{\text{g}}H_{\text{b1}}^0$  and  $\Delta_{\text{g}}H_{\text{b2}}^0$  (the relation  $\delta\Delta_{\text{g}}G^0 = \delta\Delta_{\text{g}}H^0$  is performed in gas phase) by Formulas 14 and 15, like it was done in this work (Table 2).

$$4\delta_{\text{R}}\Delta_{\text{int}}G_{\text{b1}}^0 = -(\text{PA}_{\text{H}_2\text{P}^{\text{R}_4}} - \text{PA}_{\text{H}_2\text{Por}}) = \Delta_{\text{g}}H_{\text{b1}(\text{H}_2\text{P}^{\text{R}_4})}^0 - \Delta_{\text{g}}H_{\text{b1}(\text{H}_2\text{Por})}^0 \quad (14)$$

$$4\delta_{\text{R}}\Delta_{\text{int}}G_{\text{b2}}^0 = -(\text{PA}_{\text{H}_3\text{P}^{\text{R}_4}} - \text{PA}_{\text{H}_3\text{Por}^+}) = \Delta_{\text{g}}H_{\text{b2}(\text{H}_3\text{P}^{\text{R}_4})}^0 - \Delta_{\text{g}}H_{\text{b2}(\text{H}_3\text{Por}^+)}^0 \quad (15)$$

*Meso*-phenyls show the polarity effect,<sup>[17]</sup> which heighten the proton affinity of porphyrinic platform by 2.08% and 12.71% on the first and the second protonation steps, respectively. In H<sub>2</sub>P(PhSO<sub>3</sub><sup>-</sup>)<sub>4</sub>, the  $\delta_{\text{Ph}}\Delta_{\text{int}}G_{\text{b1}}^0$  effect is increased by the negative charge of sulfonate group approximately by 30 times on the first and by 10 times on the second protonation steps. The reason for substituents effects intensification can be the expansion of isoelectronic (18  $\pi$ e) conjugation major loop from 18 to 20 atoms in series of H<sub>2</sub>P, H<sub>3</sub>P<sup>+</sup>, H<sub>4</sub>P<sup>++</sup> and, consequently, is one of the reasons for reducing the step difference  $\text{PA}_{\text{H}_3\text{P}^+} - \text{PA}_{\text{H}_2\text{P}}$  in series of H<sub>2</sub>Por, H<sub>2</sub>P(Ph)<sub>4</sub>, H<sub>2</sub>P(PhSO<sub>3</sub><sup>-</sup>)<sub>4</sub>.

**Figure 5.** Isoelectronic conjugation major loop of porphyrinic platform and its protonated forms.**Table 3.** Contributions of solvation effects in kcal/mol.

Basis	I step			II step		
	$-(\text{PA}_{\text{H}_2\text{P}} - \text{PA}_{(\text{CH}_3\text{OH})})$	$\Delta_{\text{tr}}G_1^0$	$-(\text{PA}_{\text{H}_3\text{P}^+} - \text{PA}_{(\text{CH}_3\text{OH})})$	$\Delta_{\text{g}}G_3^0$	$\Delta_{\text{g}}G_4^0$	$\Delta_{\text{tr}}G_{\text{II}}^0$
H <sub>2</sub> P	-64.55	-59.05	+9.46	-6.06	-6.35	
H <sub>2</sub> P(Ph) <sub>4</sub>	-68.92	-61.81	-7.77	-5.18	-4.38	-24.79
H <sub>2</sub> P(PhSO <sub>3</sub> <sup>-</sup> ) <sub>4</sub>	-206.64	-197.88	-150.76	-3.08	-2.17	-164.67

**Table 4.** Contributions of solvation effects in %.

Basis	I step			II step				
	$\text{PA}_{\text{CH}_3\text{OH}}$	$\Delta_{\text{tr}}G_1^0$	Sum	$\text{PA}_{\text{CH}_3\text{OH}}$	$\Delta_{\text{g}}G_3^0$	$\Delta_{\text{g}}G_4^0$	$\Delta_{\text{tr}}G_{\text{II}}^0$	Sum
H <sub>2</sub> Por	69.21	28.17	97.38	-106.98	4.47	4.68		
H <sub>2</sub> P(Ph) <sub>4</sub>	67.79	28.88	96.67	-94.92	4.15	2.86	-10.87	-98.77
H <sub>2</sub> P(PhSO <sub>3</sub> <sup>-</sup> ) <sub>4</sub>	41.25	56.35	97.60	-49.04	1.04	0.73	-51.80	-99.06

### Media Effect in Methanol

The integral media effect is made up of  $\text{PA}_{\text{CH}_3\text{OH}^+}$ ,  $\Delta_{\text{g}}G_{(\text{CH}_3\text{OH})_2}^0$ ,  $\Delta_{\text{g}}G_3^0$ ,  $\Delta_{\text{g}}G_4^0$ ,  $\Delta_{\text{tr}}G_1^0$  and  $\Delta_{\text{tr}}G_{\text{II}}^0$ .

### Proton Solvation ( $\text{PA}_{\text{MeOH}}$ )

The  $\text{PA}_{\text{MeOH}}$  value determines the acidity of solvated proton  $\text{CH}_3\text{OH}_2^+$  and, consequently, the lower bound of methanol pH scale.<sup>[11,18]</sup> The differences  $\text{PA}_{\text{H}_2\text{P}} - \text{PA}_{\text{CH}_3\text{OH}}$  and  $\text{PA}_{\text{H}_3\text{P}^+} - \text{PA}_{\text{CH}_3\text{OH}}$  show, that proton solvation ( $\Delta_{\text{g}}H_{\text{CH}_3\text{OH}_2^+}^0 = 145.07$  kcal/mol) causes the sharp decrease of protonation energy of H<sub>2</sub>P and H<sub>3</sub>P<sup>+</sup> (Tables 3 and 4). As a result, the proton transfer from  $\text{CH}_3\text{OH}_2^+$  to H<sub>3</sub>Por<sup>+</sup> becomes disadvantageous. This fact allows to explain the absence of the second protonation step of H<sub>3</sub>Por<sup>+</sup> in methanol solution.

### Formation of Solvatocomplexes $[\text{H}_4\text{P}^{++}]\text{CH}_3\text{OH}$ and $[\text{H}_4\text{P}^{++}](\text{CH}_3\text{OH})_2$ ( $\Delta_{\text{g}}G_{(\text{CH}_3\text{OH})_2}^0$ , $\Delta_{\text{g}}G_3^0$ , $\Delta_{\text{g}}G_4^0$ )

The  $[\text{H}_3\text{P}^+](\text{CH}_3\text{OH})$  complexes were not found in solutions experimentally. The calculations show, that formation of  $[\text{H}_3\text{P}^+](\text{CH}_3\text{OH})$  complexes for H<sub>2</sub>Por, H<sub>2</sub>P(Ph)<sub>4</sub> and H<sub>2</sub>P(PhSO<sub>3</sub><sup>-</sup>)<sub>4</sub> is disadvantageous in gas phase as well, where H<sub>3</sub>P<sup>+</sup>, unlike H<sub>4</sub>P<sup>++</sup>, can not tear the solvent molecule away from dimer  $(\text{CH}_3\text{OH})_2$ . H<sub>4</sub>P<sup>++</sup> form 2 solvatocomplexes  $[\text{H}_4\text{P}^{++}](\text{CH}_3\text{OH})$  and  $[\text{H}_4\text{P}^{++}](\text{CH}_3\text{OH})_2$  with similar  $\Delta_{\text{g}}G_3^0$  and  $\Delta_{\text{g}}G_4^0$  values, which is the evidence of weak guest interference effect.<sup>[2]</sup>

### Transfer into Methanol ( $\Delta_{\text{tr}}G_1^0$ and $\Delta_{\text{tr}}G_{\text{II}}^0$ )

The solvation of reagents by transfer of Reactions 5 and 9 into methanol reduces their chemical affinities and,

consequently, the energy of all chemical interactions (Tables 3 and 4). Relatively large values of  $\Delta_{tr}G_1^0$  and  $\Delta_{tr}G_{II}^0$  for  $H_2P(PhSO_3^-)_4$  are caused most likely by specific solvation of sulfonate groups. In general, media effects in methanol lower  $\Delta_g G_1^0$  and  $\Delta_g G_{II}^0$  of porphyrins by 97-99 % up to values of  $\Delta_s G_1^0$  and  $\Delta_s G_{II}^0$  typical for solutions.

#### Calculation of $K_2$ , $K_3$ and $K_4$

The transfer reduces the differences of protonation step energies of porphyrins. We took notice of the fact, that Relation 16 is constant for  $H_2P(Ph)_4$  and  $H_2P(PhSO_3^-)_4$ .

$$\frac{\Delta_s G_{II}^0 - \Delta_s G_I^0}{\Delta_g G_{II}^0 - \Delta_g G_I^0} = 0.12 \quad (16)$$

It shows that transfer into methanol lowers  $\Delta_g G_{II}^0 - \Delta_g G_I^0$  by 88% regardless of the porphyrin molecular structure. Relation 16 was used for calculation of the value  $K_2 \cdot K_3 \cdot K_4$  for  $H_2Por$ . Than, assuming that transfer equally decreases the energy properties of any elemental reaction, we used the Relation 17 to differentiate between  $K_2$ ,  $K_3$  and  $K_4$  for  $H_2Por$ ,  $H_2P(Ph)_4$  and  $H_2P(PhSO_3^-)_4$  (Table 5).

$$\frac{\lg K_i}{\lg(K_2 K_3 K_4)} = \frac{\Delta_g G_i^0}{\Delta_g G_2^0 + \Delta_g G_3^0 + \Delta_g G_4^0} \quad (17)$$

**Table 5.** Constants of I and II protonation steps of porphyrins in methanol.

Porphyrin	$\lg K_1$	$\lg K_2$	$\lg K_3$	$\lg K_4$	$\lg K_2 - \lg K_1$
$H_2Por$	4.98	1.17	-0.87	-0.91	-3.81
$H_2P(Ph)_4$	6.16	0.72	0.41	0.35	-5.44
$H_2P(PhSO_3^-)_4$	7.37	2.88	0.06	0.04	-4.49

To verify the calculated  $K_1$ ,  $K_2$ ,  $K_3$  and  $K_4$  values, we made the simulation dependences (Equations 18-23) of

concentration current value of  $H_3P^+$ ,  $H_4P^{++}$ ,  $[H_4P^{++}](CH_3OH)$  and  $[H_4P^{++}](CH_3OH)_2$  on pH of porphyrin solutions in methanol (Figure 6) and compared them with the experimental ones (Figures 1b, 2b, 3b).

$$C_{H_2P} = \frac{1}{\sum_{i=1}^{n=5} C_i} \cdot 100\% \quad (18)$$

$$C_{H_3P^+} = \frac{K_1 \cdot 10^{-pH}}{\sum_{i=1}^{n=5} C_i} \cdot 100\% \quad (19)$$

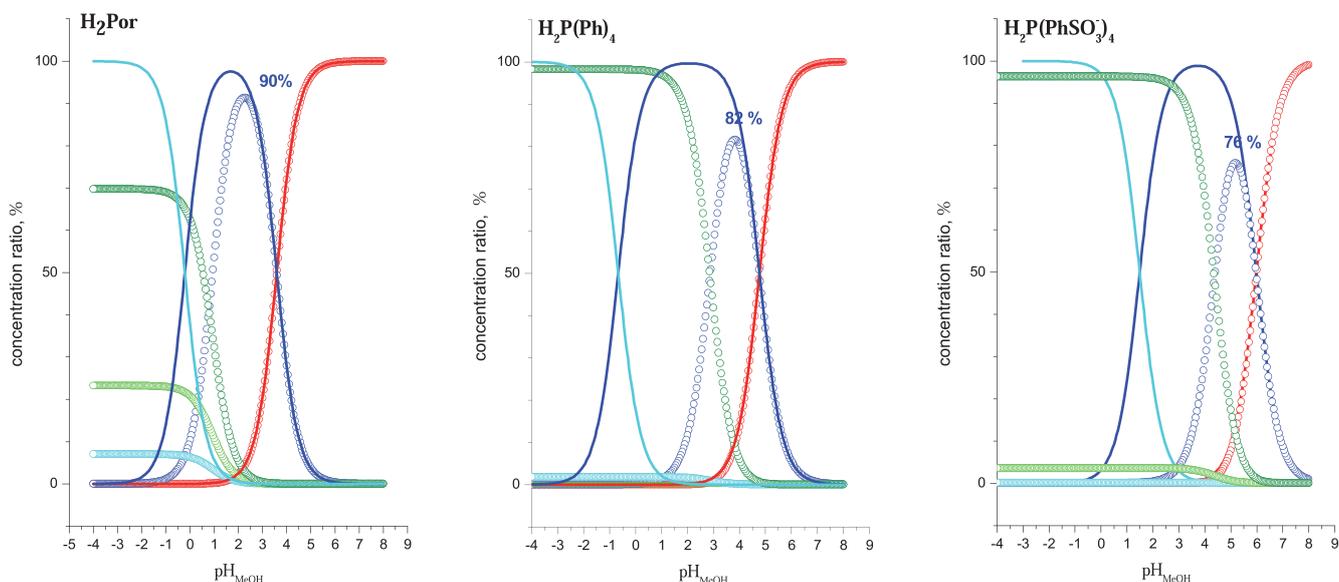
$$C_{H_4P^{++}} = \frac{K_1 \cdot K_2 \cdot 10^{-2pH}}{\sum_{i=1}^{n=5} C_i} \cdot 100\% \quad (20)$$

$$C_{[H_4P^{++}](CH_3OH)} = \frac{K_1 \cdot K_2 \cdot K_3 \cdot 10^{-2pH} \cdot C_s}{\sum_{i=1}^{n=5} C_i} \cdot 100\% \quad (21)$$

$$C_{[H_4P^{++}](CH_3OH)_2} = \frac{K_1 \cdot K_2 \cdot K_3 \cdot K_4 \cdot 10^{-2pH} \cdot C_s^2}{\sum_{i=1}^{n=5} C_i} \cdot 100\% \quad (22)$$

$$\sum_{i=1}^5 C_i = 1 + K_1 \cdot 10^{-pH} + K_1 \cdot K_2 \cdot 10^{-2pH} + K_1 \cdot K_2 \cdot K_3 \cdot 10^{-2pH} \cdot C_s + K_1 \cdot K_2 \cdot K_3 \cdot K_4 \cdot 10^{-2pH} \cdot C_s^2 \quad (23)$$

In the case of  $H_2Por$  the maximal concentration of  $H_3P^+$  (Figure 6,  $H_2Por$ ,  $n=5$ ) reaches only 89% (2.40 pH) compared to 97% in the experiment. The observed divergence can be explained by sharp deviate of the real experimental system properties from model on the edge of methanol acidity. For  $H_2P(Ph)_4$  and  $H_2P(PhSO_3^-)_4$  simulation dependences (Figure 6,  $H_2P(Ph)_4$  and  $H_2P(PhSO_3^-)_4$  at  $n=5$ ) agree ideally with the experimental ones, showing, that equilibriums of the second protonation step of these porphyrins practically are totally



**Figure 6.** Simulation dependences corresponding to Equations 18-22:  $H_2P$  (red),  $H_3P^+$  (blue),  $H_4P^{++}$  (cyan),  $[H_4P^{++}](CH_3OH)$  (green),  $[H_4P^{++}](CH_3OH)_2$  (dark green). Points  $n=5$ , lines  $n=3$ .

shifted to  $[H_4P^{++}](CH_3OH)_2$  because of the big concentration (activity) of the solvent in the solution, just as we supposed in the beginning of this work.

For graphic illustration of the media effects, we made hypothetical dependences (18-20), neglecting the formation of solvatocomplexes  $[H_4P^{++}](CH_3OH)$  and  $[H_4P^{++}](CH_3OH)_2$  (Figure 6,  $n=3$ ). These dependences (solid lines) show, that without complexing the concentration of  $H_3P^+$  reaches 100% in all cases and, consequently, the titration curves would be two-step. But in the methanol pH scale we would observe only the first step of protonation of  $H_2P(Ph)_4$  and the half of the second one for  $H_2P(PhSO_3^-)_4$ .

## Conclusions

The diprotonated porphyrinic platform  $H_4P^{++}$  is a molecular receptor and bundles up the methanol molecules, forming the solvatocomplexes  $[H_4P^{++}](CH_3OH)$  and  $[H_4P^{++}](CH_3OH)_2$ . The equilibriums of the second protonation step of  $H_2P$  composed of 5,10,15,20-tetraphenylporphin and 5,10,15,20-tetrakis(4'-sulfonatophenyl)porphin practically are totally shifted to solvatocomplexes  $[H_4P^{++}](CH_3OH)_2$ . This effect is the reason for levelling the step protonation constants of porphyrins, measured by spectrophotometric method, which "doesn't distinguish" the light-absorbing centers  $H_4P^{++}$ ,  $[H_4P^{++}](CH_3OH)$  and  $[H_4P^{++}](CH_3OH)_2$ .

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