Effect of p*H* on Formation of Metalloporphyrins

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Although complexation reactions of porphyrins with metal salts in organic solvents have a long research history, the influence of pH on these processes was not studied. The main reason is complications connected with the pH measurements in nonaqueous solutions. To solve this problem the special instrumentation was created for application of the spectropotentiometric method (spectroscopy + p*H*-metry with glass electrode) in nonaqueous solutions. Using this method it became possible to investigate complexation reactions at different pH values using electronic absorption spectroscopy. The p*H* control of reaction systems allows us to explain the peculiarities of metalloporphyrins formation without invoking the Fleischer's idea o*f* SAT-complexes.

Introduction

Substituted derivatives of 21*H*,23*H*-porphine (H_2P) are named porphyrins (H_2L). Due to the presence in the coordination cavity of the porphyrin macrocycle of two types of activity centers (acidic imino-groups and basic aza-atoms) porphyrins are amphoteric and can produce in the protolytic reactions four types of ionic species L^{2-}, HL^-, H_3L^+ и H_4L^{2+} according to Equilibria (1)-(4) which are correct for polar solvents (*S*):

$$H_2L \xleftrightarrow{K_{a1}} HL^- + H^+ \qquad (1)$$

$$HL^- \xleftrightarrow{K_{a2}} L^{2-} + H \qquad (2)$$

$$H_2L + H^+ \xleftrightarrow{K_{b1}} H_3L^+ \qquad (3)$$

$$H_3L^+ + H^+ \xleftrightarrow{K_{b1}} H_4L^{2+} \qquad (4)$$

Due to the double positive charge and presence of four endocyclic NH-groups which are hydrogen bonds donors, the dication H_4L^{2+} in contrast to H_2L and H_3L^+ exhibits properties of the anion-molecular receptor.[1,2,3] In solutions H_4L^{2+} exists only in the form of supramolecular homogeneous and heterogeneous complexes with solvent molecules and background anions - $H_4L^{2+}S_2$, $H_4L^{2+}S(X^-)$ and $H_4L^{2+}(X^-)_2$.

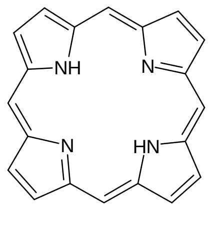
Equilibria (1)-(4) cover a wide p*H* range. Deuteroporphyrin IX dimethyl ester (H_2DP) is the only porphyrin for which both acid and base ionization constants have been reliably determined in one solvent (DMSO). The difference between K_{a1} and K_{b1} exceeds 24 orders of magnitude. Constants of the Equilibria (1)-(4) for H_2DP and some other porphyrins are presented in Table 1.

Substitution of two endocyclic hydrogen atoms in porphyrins by a metal cation leads to metalloporphyrins. In these complexes, *e.g.* $M^{II}L$, porphyrins can be considered as dianionic tetradentate ligands. The reactivity of the ionic forms of porphyrins in complexation with metal cations decreases in the order $L^{2-} > HL^- > H_2L > H_3L^+ > H_4L^{2+} > H_4L^{2+}S(Hal^-) > H_4L^{2+}(Hal^-)_2$. Therefore acid-base properties of porphyrins and p*H* of the medium should have a strong influence on the mechanism of metalloporphyrin formation.

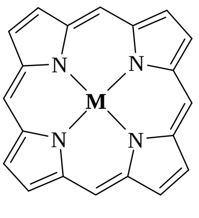
Complexes of Cd^{2+} with "acidic" porphyrazine, H_2PA, and its derivatives are formed in System (5) as a result of interaction between the metal ion and the most reactive form of ligand (L^{2-}) according to Equilibrium (6):[5].

$$Cd(Ac)_2 - H_2L - HClO_4 - DMSO \qquad (5)$$

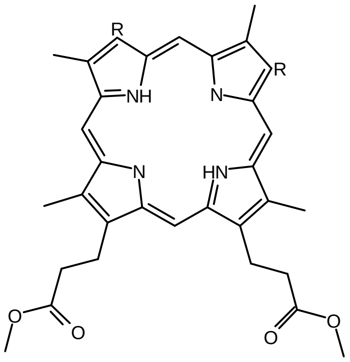
$$L^{2-} + Cd^{2+} \xleftrightarrow{Kst} CdL \qquad (6)$$



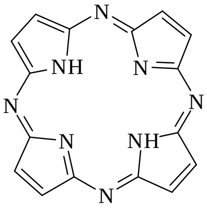
H_2P



$M^{II}P$



H_2DP (R= H)
H_2MP(R= C_2H_5)
H_2PP(R= CH=CH_2)



H_2PA

Table 1. Constants of Equilibria (1)-(4) measured by spectropotentiometric method at 298 K.

Solvent	ε	DN	K_i	H_2PA	H_2P	H_2DP	H_2MP
Dimethyl-sulfoxide (DMSO)	46.68	29.8	pK_{a1}	11.94 ± 0.04 [4,5]	22.35 ± 0.02 [6]	25.30 [9,10]	
			pK_{a2}	13.45 ± 0.08 [4,5]			
			lgK_{b1}			0.87 ± 0.03 [8]	1.48 ± 0.03 [8]
			lgK_{b2}			0.04 ± 0.03 [8]	0.65 ± 0.03 [8]
Acetonitrile (AN)	36.02	14.1	lgK_{b1}		9.15 ± 0.15 [7]	9.17 ± 0.03 [8]	11.95 ± 0.05 [1]
			lgK_{b2}		6.20 ± 0.15 [7]	5.80 ± 0.03 [8]	7.51 ± 0.05 [1]

The H_2PA molecules are ionized partly even in pure DMSO (p$H \approx 10$) – the quota of $[HPA^-]$ and $[PA^{2-}]$ is 1.14 and $4\cdot10^{-4}$ %, respectively. As a result Equilibrium (6) is completely displaced to the right side and the complexes of porphyrazines are formed instantaneously upon mixing of reagents. Equilibrium (6) can be observed only in acidified solutions of DMSO when only H_2L and CdL are seen in the electronic absorption spectra of System (5) and Equilibrium (7) can be studied. The stability constant K_{st} can be derived from Equation (8).

$$H_2L + Cd^{2+} \xleftrightarrow{Ke} CdL + 2H^+ \qquad (7)$$

$$K_e = K_{st}K_{a1}K_{a2} \qquad (8)$$

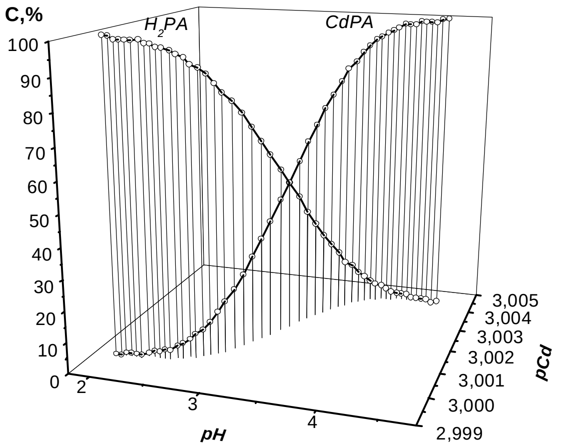


Figure 1. Equilibrium composition observed for H_2PA in System (5) at 298 K.

Figure 1 shows equilibrium composition for System (5) in the case of H_2PA. In the point of half-conversion the equilibrium concentration of $[PA^{2-}]$ is only $6.38\cdot10^{-25}$ M and its quota is $6.38\cdot10^{-18}$ %. Nevertheless, Equilibrium (7) in System (5) is achieved very quickly and has the rates comparable with that usual for protolytic processes. The constants of true and formal kinetic Equations (9) and (10) describing formation of CdL are connected by Equation (11).

$$V = k\,[M^{2+}][L^{2-}] \qquad (9)$$

$$V = k'\,[M^{2+}][H_2L] \qquad (10)$$

$$k' = kK_{a1}K_{a2}/[H^+]^2 \qquad (11)$$

Common porphyrins (H_2P and its derivatives obtained by substitution of exocyclic hydrogen atoms), have much weaker acidic properties than porphyrazines - the difference in the K_{a1} values is more that 11 orders of magnitude. In this case the neutral form H_2L was postulated as the reactive particle in the complex formation.[11-13] In neutral DMSO at overall concentration of H_2L $1\cdot10^{-5}$ M the equilibrium concentration of $[L^{2-}]$ is not exceeded 10^{-33} M. In addition, the mechanisms and conditions of formation and dissociation of common porphyrin complexes are different.[14] Because of that complexation reaction of common porphyrins (12) proceeds slowly and irreversibly:

$$H_2L + M^{2+} \xrightarrow{K_V} ML + 2H^+ \qquad (12)$$

It is assumed that positively charged protonated forms of common porphyrins H_3L^+ and H_4L^{2+} can not be coordinated by metal cations.[14-17] It should be noted that information about structure and reactivity of solvato-complexes of metal ions in nonaqueous solutions at different acidity is absent.

Though Reaction (12) is pH-dependent, the influence of the solution acidity on the complexation kinetics of porphyrins has never been previously studied. The main reason is complication of pH measurements in nonaqueous solutions. To solve this problem we have elaborated the equipment for spectropotentiometric titration (spectroscopy + pH-metre with glass electrode)[18,19] in nonaqueous solutions. This enables the investigation of the pH influence on complexation equilibrium using electronic absorption spectroscopy. Results of the spectropotentiometric investtigation of the influence of solution acidity on Reaction (12) between the neutral form of porphyrins and metal ions in Systems (13) and (14) are reported in this paper.

$$H_2MP – Cu(NO_3)_2\cdot3H_2O – DMSO \qquad (13)$$

$$H_2MP – Cu(NO_3)_2\cdot3H_2O – HClO_4 – DMSO \qquad (14)$$

Experimental

Reagents

Mesoporphyrin IX dimethyl ether (H_2MP) was prepared according to the known method[20] and purified by column chromatography on alumina (II degree of activity by Brockmann, eluent – chloroform). Purity of the product was controlled by electronic absorption spectra.

Chemically pure DMSO was kept over NaOH for 24 hours and distilled in vacuum (2-3 mmHg).[21] Residual amount of water was 0.2267%. Chemically pure $HClO_4\cdot3.5H_2O$ was used without additional purification. Analytically pure $Cu(NO_3)_2\cdot3H_2O$ was prepared as described elsewhere.[22] Pure Et_4NCl was recrystallized twice from dry acetonitrile and dried during 24 hours under vacuum (0.01 mmHg) at room temperature. Et_4NClO_4

was prepared by precipitation as result of mixing chemically pure $HClO_4 \cdot 3.5H_2O$ with purified Et_4NCl. After that it was recrystallized from glacial distilled water and dried 24 hours under vacuum (0.01 mmHg) at room temperature.

Measurements

Measurements were pursued with the specially designed spectropotentiometric cell (Figure 2).

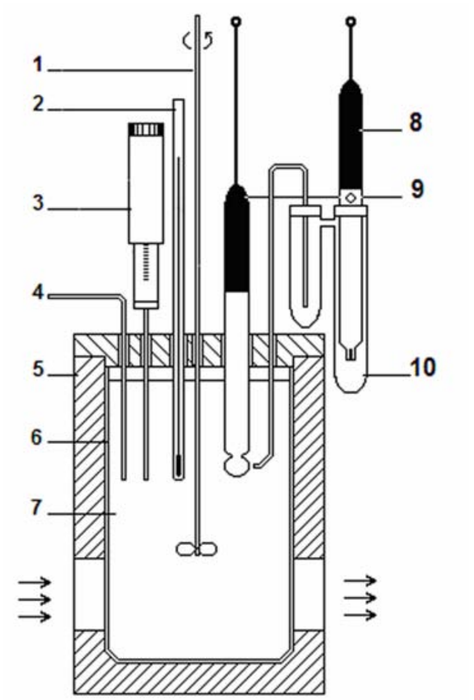


Figure 2. Spectropotentiometric cell (1 - rabble; 2 - mercury thermometer; 3 - microsyringe with titrant; 4 - gas feed capillary; 5 - thermostat; 6 - optical cell; 7 - work solution; 8 - reference electrode; 9 - glass electrode; 10 - electrolytic bridge)

Electronic absorption spectra were measured with spectrophotometer Agilent 8453. Potentiometric measurements (accuracy 1 mV) were carried out with Element (15), using p*H*-meter OP 211, glass electrode EGL-43-07 (GE) and silver chloride reference electrode filled with Et_4NCl in DMSO.

↓↓↓

Ag	AgCl	saturated solution of Et_4NCl in DMSO	0,01 M solution Et_4NClO_4 in DMSO	System (13) or (14)	GE	(15)

↓↓↓

To separate the investigated solution from chloride ions the reference electrode was supplied by the electrolytic bridge filled with 0.01 M solution of Et_4NCl in DMSO. The glass electrode was kept in water. It was washed with DMSO and drained with filter paper before each measurement. The temperature of the solution was maintained with accuracy ± 0.1°C using liquid thermostate.

Graduation of the Element for pH Measurements in DMSO.

Graduation of the glass electrode was carried out with buffer solutions in DMSO (Table 2.).

Table 2. The p*H* values of buffer solutions in DMSO in the temperature range 298 – 318 K.[18,23]

Composition (1:1)	*C*, M	p*H*
picric acid + it's lithium salt	0.05	$1.10 - 0.005(T - 298)$
salicylic acid + it's sodium salt	0.05	$6.05 - 0.010(T - 298)$
2- nitrobenzoic acid + it's sodium salt	0.05	$7.16 - 0.001(T - 298)$
benzoic acid + it's sodium salt	0.05	$9.60 - 0.003(T - 298)$

Kinetic Experiment

Reaction (12) was investigated in systems **I**, **II**, **III**, **IV**, **V** and **VI** (Table 3). To 75 ml of the p*H*-neutral or acidified H_2MP solution 3 ml of the concentrated solution of $Cu(NO_3)_2 \cdot 3H_2O$ was added and following changes of p*H* and electronic absorption spectra were registered.

Calculations

Values of [CuMP] and $[H_2MP]$ were calculated using Equations (16)-(18).

$$C_{H2MP} = [CuMP] + [H_2MP] + [H_3MP^{+}] + [H_4MP^{2+}(DMSO)_2] \quad (16)$$

$$A_T = [CuMP] \cdot \varepsilon_{(CuMP)} l + \frac{(C_{H_2MP} - [CuMP]) \cdot l}{1 + K_{b1} a_{H^+} + K_{b1} K_{b2} a_{H^+}^2} \times$$
$$\cdot \times \left[\varepsilon_{CuMP} + K_{b1} a_{H^+} \varepsilon_{H_3MP^+} + K_{b1} K_{b2} a_{H^+}^2 \cdot \varepsilon_{H_4MP^{2+}(DMSO)_2} \right] \quad (17)$$

$$[H_2MP] = \frac{C_{H_2MP} - [CuMP]}{1 + K_{b1} a_{H^+} + K_{b1} K_{b2} a_{H^+}^2} \quad (18)$$

where C_{H2MP} - general concentration of porphyrin, M; A_T – current value of optical density ; ε_i –molar absorption coefficient at analytical wave-length; $a_{H+} = 10^{-pH}$; K_{b1} and K_{b2} – constants of Reactions (3) and (4); l – thickness of absorbent layer, cm.

Table 3. Initial conditions of kinetic experiments for reaction systems **I-VI** at 318K.

System	(13)			(14)		
	I	**II**	**III**	**IV**	**V**	**VI**
pH_0	9.99	9.99	9.99	3.01	1.31	0.61
C_{H2MP}[a]	$3.38 \cdot 10^{-5}$	$2.78 \cdot 10^{-5}$	$2.98 \cdot 10^{-5}$	$2.98 \cdot 10^{-5}$	$3.01 \cdot 10^{-5}$	$3.04 \cdot 10^{-5}$
$C_{Cu(NO3)2 \cdot 3H2O}$[a]	$2.90 \cdot 10^{-2}$	$1.45 \cdot 10^{-2}$	$2.90 \cdot 10^{-3}$	$2.98 \cdot 10^{-3}$	$2.98 \cdot 10^{-3}$	$2.98 \cdot 10^{-3}$

[a] - analytical concentration in M at 298K

Results and Discussions

Solvolysis of $Cu(NO_3)_2{\cdot}3H_2O$ in DMSO

Addition of $Cu(NO_3)_2{\cdot}3H_2O$ in p*H*-neutral DMSO leads to drastic decrease of p*H* (Figure 3).

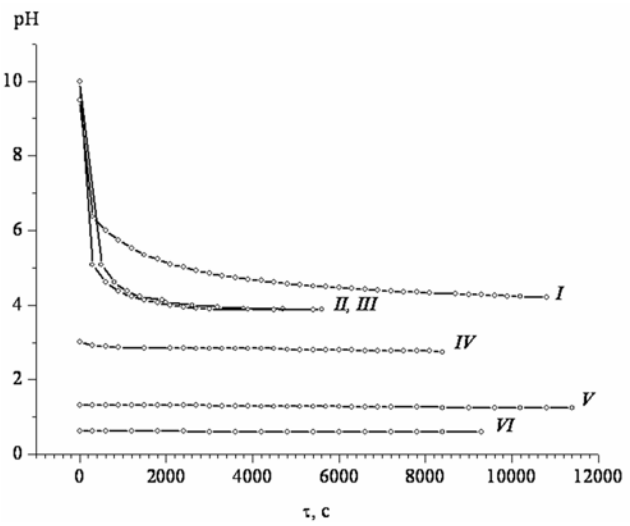


Figure 3. Changes of p*H* in systems **I-VI** at 318 K.

Figure 4 shows the p*H* dependence from concentrations of $Cu(NO_3)_2{\cdot}3H_2O$ and $HClO_4$ which was used to determine acidity of $Cu(NO_3)_2{\cdot}3H_2O$ in DMSO. Both dependencies belong to one straight line which obeys Equation (19) with the correlation factor 0.9997.

$$pH = -\,1.241{\cdot}\lg C + 2.91;\quad N=56 \qquad (19)$$

Under such experimental conditions the $Cu(NO_3)_2{\cdot}3H_2O$ is strong one-basic acid. The complex $Cu^{2+}(OH^-)(DMSO)_5$ is a product of the salt solvolysis.[24] Moreover, in the case of non-hydrated copper(II) salt the complex $Cu^{2+}(OH^-)(DMSO)_5$ might be a product of interactions with residual water.

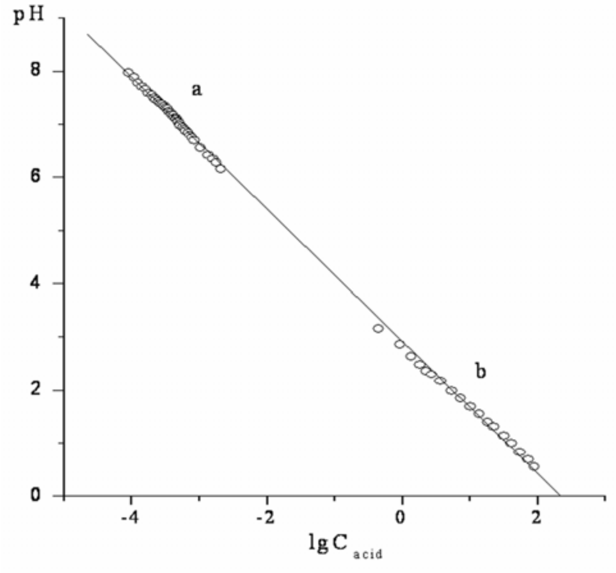


Figure 4. Dependence of p*H* from the concentrations of $Cu(NO_3)_2{\cdot}3H_2O$ (a) and $HClO_4$ (b) in DMSO at 298 K.

Protonation of H_2MP in DMSO

Protonation of H_2MP according to Equilibria (3) and (4) was investigated in System (20) at 298-318 K.[8]

$$H_2MP\text{–}HClO_4\text{– DMSO} \qquad (20)$$

As it has been shown, the porphyrinium dication $H_4MP^{2+}(DMSO)_2$ exhibits properties of the anion molecular receptors.[1-3] In the system (20) the equilibrium (21) is completely displaces to the right side while formation of complexes with H_2O, ClO_4^- and NO_3^- are suppressed with excess of solvent.

$$H_4MP^{2+} + 2DMSO \xleftrightarrow{K_{st}} H_4MP^{2+}(DMSO)_2 \qquad (21)$$

It has been shown[8] that increase of stability of the porphyrin solvatocomplex leads to levelling of K_{b1} and K_{b2} values. The value of $\lg(K_{b1}/K_{b2})$ is equal to 0.83 for H_2MP in DMSO and to 4.44 in acetonitrile under the same conditions (at 298 K). Generally, both Equilibria (3) and (4) are overlapped at $\lg(K_{b1}/K_{b2}) < 4$.[25] The constants of acid dissociation of H_2MP in DMSO are unknown. Value of pK_{a1} for H_2MP in DMSO should be higher than that for H_2DP (pK_{a1}=25.30 in DMSO at 298 K[9,10]) in which two ethyl radicals are absent. Equilibrium structure of the System (17) was calculated using Equations (22)-(25) at the p*H* range from – 2.5 to 4.0 (Figure 5) ignoring the equilibrium concentrations of HMP^- and MP^{2-}.

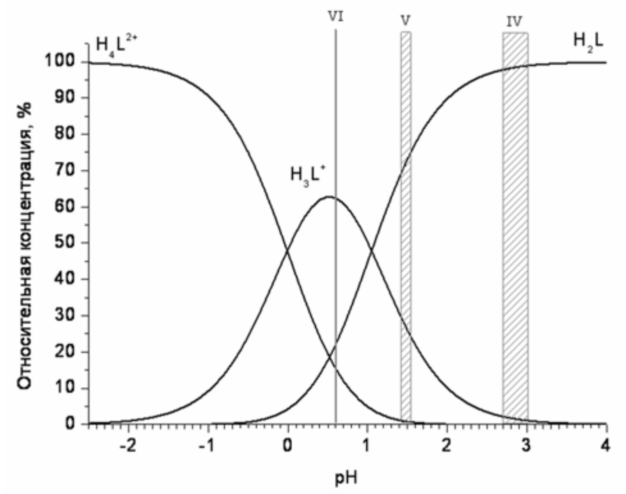


Figure 5. Dependences of equilibrium concentrations from p*H* in System (20)

$$C_{H2MP} = [H_2MP] + [H_3MP^+] + [H_4MP^{\,2+}(DMSO)_2] \qquad (22)$$

$$[H_2MP] = \frac{100\%}{1 + K_{b1}\cdot a_{H^+} + K_{b1}\cdot K_{b2}\cdot a_{H^+}^2} \qquad (23)$$

$$[H_3MP^+] = K_{b1}\cdot a_{H^+}\cdot[H_2MP] \qquad (24)$$

$$[H_4MP^{2+}(DMSO)_2] = K_{b1}\cdot K_{b2}\cdot a_{H^+}^2\cdot[H_2MP] \qquad (25)$$

In Figure 5 it is possible to allocate areas corresponding individual step of Equilibrim (3) at p*H* > 1.7 and Equilibrim (4) at p*H* < – 1.5, while at 1.7 > p*H* > – 1.5 both Equilibria (3) and (4) are overlapped. In the electronic absorption spectra (Figure 6) the equilibria between pairs of light-absorbing species H_2MP; H_3MP^+ and H_3MP^+; $H_4MP^{2+}(DMSO)_2$ correspond to individual series of isosbestic points at 462; 512; 612 and 537; 558; 609 nm, respectively. The isobestic points are not observed in the area of the triple equilibrium between H_2MP, H_3MP^+ and $H_4MP^{2+}(DMSO)_2$.

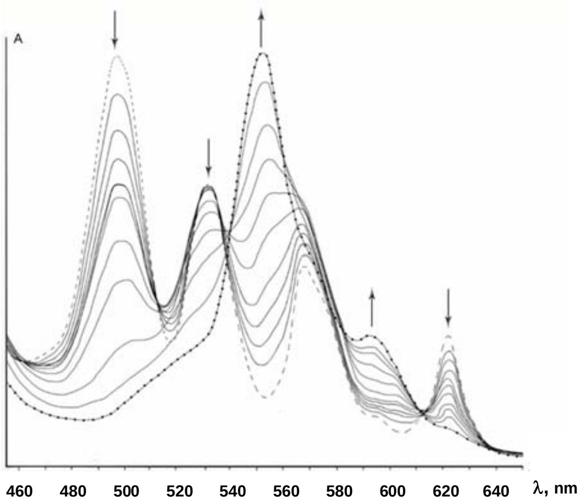


Figure 6. Changes of electronic absorption spectra in System (20) in the p*H* range from -2.5 to 4.0 at 318 K; (– –) H_2MP; (–•–) $H_4MP^{2+}(DMSO)_2$.

*Kinetics of Complex Formation in Reaction Systems **I** - **VI***

Solvolysis of $Cu(NO_3)_2{\cdot}3H_2O$ in DMSO leads to acidification of solution (26):

$$Cu(NO_3)_2{\cdot}3H_2O + 5DMSO \rightarrow$$
$$Cu^{2+}(OH^-)(DMSO)_5 + 2H_2O + 2NO_3^- + H^+ \qquad (26)$$

Parameters of the investigated kinetic systems with allowance made for solvolysis are presented in Table 4.

Self acidification observed in systems **I-III** does not lead to protonation of H_2MP, which occurs only at lower values of p*H*. Therefore the porphyrin exists only in the molecular form and all changes of the electronic absorption spectra are caused only by changes of concentrations of H_2MP and CuMP (Figure 7). One series of isobestic points at 510 and 576 nm is in agreement with them. In these isobestic points Equation (27) is fulfilled.

$$A = \varepsilon_i{\cdot}l{\cdot}([H_2MP] + [CuMP]) \qquad (27)$$

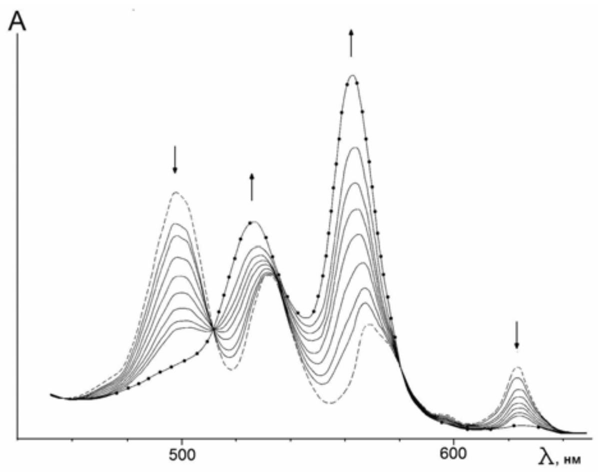


Figure 7. Changes of electronic absorption spectra in Systems **I-IV** (Table 4): (– –) H_2MP at p*H* 9.99; (–•–) CuMP at p*H* 4.00 – 2.71.

The presence of the isobestic points indicates the absence of other light-absorbing forms of porphyrin, such as sitting-atop (SAT) complexes.[13,26] The formation of CuMP was studied at the constant concentration of H_2MP and various excesses of $Cu(NO_3)_2{\cdot}3H_2O$ in systems **I**–**IV**. The reaction obeys the linear kinetic Equation (28) and is characterized by the pseudo-first order rate law in H_2MP.

$$\ln([H_2MP]_0 / [H_2MP]) = k_{ef}{\cdot}\tau \qquad (28)$$

The parameters of the kinetic dependence (28) are presented in Table 4 and Figure 8.

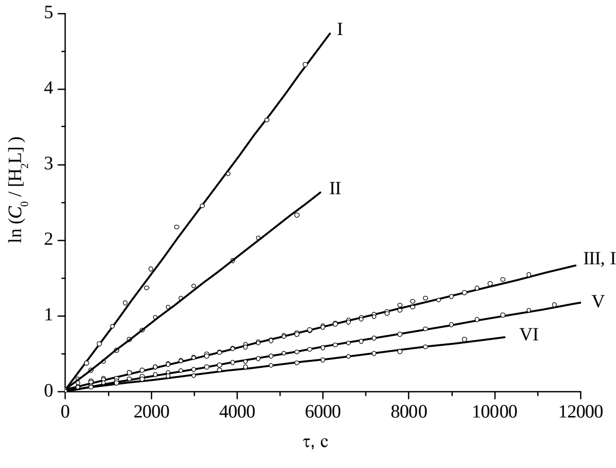


Figure 8. Kinetic dependences of Reaction (12) in systems **I** – **VI**.

Table 4. Parameters of reaction systems **I** – **VI** with regard to solvolysis of $Cu(NO_3)_2{\cdot}3H_2O$ and protonation of H_2MP

System	(13)			(14)		
	I	**II**	**III**	**IV**	**V**	**VI**
Range of p*H*	9.99- 3.87	9.99- 3.87	9.99- 4.00	3.01- 2.71	1.31- 1.23	0.61- 0.60
$[H_2MP]_0$[a]	$3.38{\cdot}10^{-5}$	$2.78{\cdot}10^{-5}$	$2.98{\cdot}10^{-5}$	$2.89{\cdot}10^{-5}$	$1.93{\cdot}10^{-5}$	$0.69{\cdot}10^{-5}$
(% of C_{H2MP})	(100)	(100)	(100)	(98.91)	(64.01)	(22.75)
$C_{Cu(DMSO)_5OH^+}$	$2.90{\cdot}10^{-2}$	$1.45{\cdot}10^{-2}$	$2.90{\cdot}10^{-3}$	$2.98{\cdot}10^{-3}$	$2.98{\cdot}10^{-3}$	$2.98{\cdot}10^{-3}$
R (Figure 5)	0,999	0,999	0,999	0,999	0,999	0,997
lg k_{ef} (318 K)	-3.12	-3.36	-3.86	-3.86	-4.01	-4.17
lg k_v (318 K)			2.95±0.04			

[a] equilibrium concentration, M (at 298 K).

The system IV was investigated at initial p*H* = 3 (beginning of protonation of H_2MP) when total equilibrium content of H_3MP^+ and $H_4MP^{2+}(DMSO)_2$ is 1% and the results of kinetic measurements can not be influenced. This value of p*H* was only one unit less then that at the end of $Cu(NO_3)_2{\cdot}3H_2O$ solvolysis. The acidification sharply narrows the interval of p*H* change to 0.3 units (Figure 5). As has been shown above the salt $Cu^{2+}H_2O(DMSO)_5$ is a strong one-basic acid in DMSO. This conclusion was proved by full coincidence of kinetic dependences for systems **III** and **IV**.

Spectral changes in the system **VI** are shown in Figure 9. The equilibrium mixtures of H_2MP, H_3MP^+ and $H_4MP^{2+}(DMSO)_2$ (Figure 5) were investigated under initial conditions (Table 4). The p*H* changes in systems **V** and **VI** are very small.

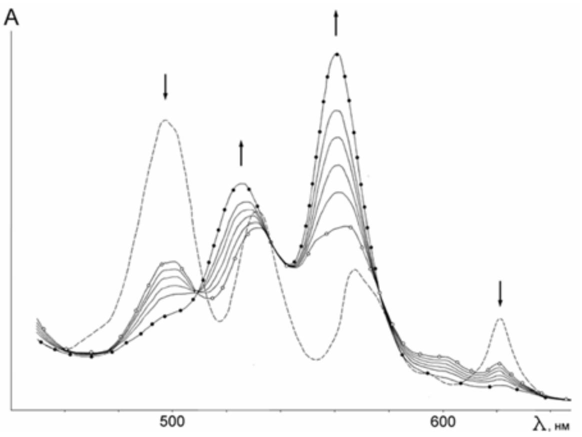


Figure 9. Changes of electronic absorption spectra of system **VI** (Table 4). (– –) H_2MP at p*H* 9.99; (–○–) initial equilibrium mixture H_2MP, H_3MP^+, $H_4MP^{2+}(DMSO)_2$ at p*H* 0.61; (–●–) CuMP at p*H* 0.60.

At the constant value of p*H* the ration of components in the equilibrium mixture H_2MP, H_3MP^+ and $H_4MP^{2+}(DMSO)_2$ is constant (Figure 5). The electronic absorption spectra of such mixtures can be similar to that of individual substances. The formation of CuMP is characterized by the same isobestic points at 510 and 576 nm (Figure 9) in systems I – VI. Thus the only reactive form of the ligand is H_2MP. In systems I – III the formation of CuMP was studied at various excesses of salt and constant H_2MP concentration. In systems IV, V and VI it was studied at constant concentration of $Cu(NO_3)_2{\cdot}3H_2O$ taken in excess and various concentrations of the porphyrin ligand.

In all these systems the reaction obeys linear kinetic Equation (28) and it is characterized by pseudo-first order rate law in H_2MP. The dependences of effective constant of Reaction (29) from the concentration of the salt $Cu(NO_3)_2{\cdot}3H_2O$ (in Systems **I-IV**) and on the concentration of H_2MP (in Systems **IV-VI**) were obtained. In the case of the first order in salt, effective k_{ef} and true k_v constants can be connected by linear Equation (30). It was experimentally confirmed that this equation is correct for all investigated Systems **I-VI**.

$$Cu^{2+}(OH^-)(DMSO)_5 + H_2MP \rightarrow$$
$$\rightarrow CuMP + H_2O + H^+ + 5DMSO \quad (29)$$

$$k_{ef} = k_v\,[H_2MP][Cu^{2+}(OH^-)(DMSO)_5] \quad (30)$$

The experimental dependence of k_{ef} from $[H_2MP][Cu^{2+}(OH^-)(DMSO)_5]$ (Equation (31)) have the correlation coefficient *R* = 0.9998 (Figure 10).

$$k_{ef} = (884.66 \pm 9.47)[H_2MP][Cu^{2+}(OH^-)(DMSO)_5] \quad (31)$$

The value of k_v in Equation (30) is equal 884.66 ± 9.47 at 318 K (lg k_v = 2.95±0.04).

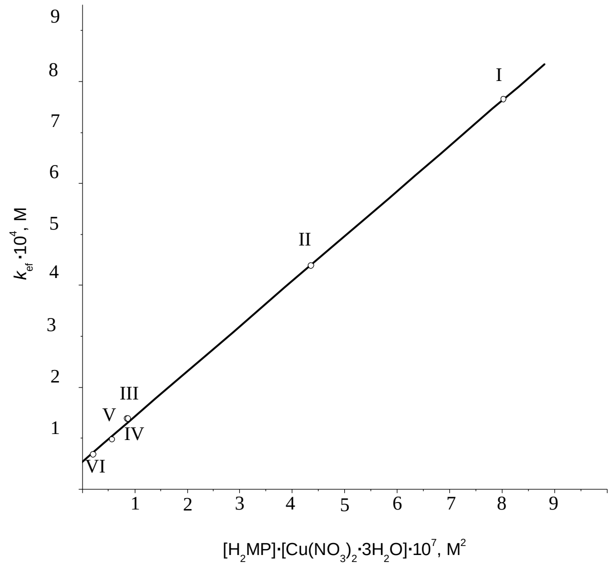


Figure 10. Correlation between k_{ef} and $[H_2MP][Cu^{2+}(OH^-)(DMSO)_5]$ for Reaction (29) in Systems **I**–**VI** at 318 K.

Fleischer's SAT-complex

The porphyrinium dications H_4L^{2+} have properties of p*H*-dependent anion-molecular receptors. They are formed due to sequential protonation coordination cavity of porphyrin macrocycle by two proton. The second proton activates porphyrinium receptor H_4L^{2+} and starts up self-assembling of anion-molecular complexes $H_4L^{2+}S_2$, $H_4L^{2+}SB$ и $H_4L^{2+}B_2$ (B – molecular or anion substrate). The composition and stability of these complexes are determined by each reaction system.

$$H_4L^{2+}S_2 + B \overset{K_{d1}}{\longleftrightarrow} H_4L^{2+}SB + S \quad (32)$$

$$H_4L^{2+}SB + B \overset{K_{d2}}{\longleftrightarrow} H_4L^{2+}B_2 + S \quad (33)$$

Generally, values of K_{b1}, K_{b2}, K_{d1}, K_{d2} exhibit antibathic dependencies from basicity (DN) and polarity (ε) of solvents In highly basic and polar DMSO (reaction System (14)) the dication H_4MP^{2+} exists as molecular complex $H_4MP^{2+}(DMSO)_2$. Because of small values of K_{b1} and K_{b2} (Table 1), large excess of acid is necessary for formation of H_4MP^{2+} in DMSO. The values of K_{b1} and K_{b2} are increased by ten and seven of orders magnitude in going from DMSO to moderately basic and polar acetonitrile (AN). The dication H_4MP^{2+} is characterized by high selectivity to halide-ions. As it can be seen (Table 5), the complexes $H_4MP^{2+}(AN)(Hal^-)$ and $H_4MP^{2+}(Hal^-)_2$ are very stable. Due to the formation of $H_4MP^{2+}(Cl^-)_2$ in acetonitrile the energy of stabilization of H_4MP^{2+} achieves 54.4 kJ/mol.

Table 5. Constants of Equilibriums (32) and (33) in system $H_2MP - HClO_4 - B$ –acetonitrile at 298 K

$\lg K_i$	Substrate (B)				
	ClO_4^- [3] a	H_2O [27]	I^- [27]	Br^- [27]	Cl^- [27]
$\lg K_{d1}$	<<1	0.93±0.08	4.27±0.02	5.13±0.01	5.24±0.02
$\lg K_{d2}$	<<1	0.52±0.05	2.83±0.01	3.31±0.03	4.29±0.03

[a] SCN^-, NO_3^-, HSO_4^-, IO_3^-, CH_3COO^- [28]

Complexes $H_4MP^{2+}(AN)(Hal^-)$, $H_4MP^{2+}(Hal^-)_2$ and $H_4MP^{2+}(AN)_2$ have very similar electronic absorption spectra.

Solvents with weak polarity (for example chloroform) are characterized by smaller DN and ε values in comparison with acetonitrile. Obviously, the stability of the complexes of porphyrin dications with halogens will be higher in such solvents. This fact allows us to interpret the data obtained in System (34) by Fleischer [26] in a new way.

$$H_2PP - FeCl_3 - CHCl_3 \qquad (34)$$

In this system instead of the Fe^{III} complex $ClFe^{III}PP$ a stable species is formed which was named the SAT-complex. It is characterized by electronic absorption spectrum which strongly resembles the spectrum of H_4PP^{2+}. Addition of such bases as pyridine and ethanol destroys the SAT-complex with appearance of the molecular form H_2PP. This SAT-complex was considered as a mixed complex $FeCl_3{\cdot}H_2PP$. This conclusion did not take into account self-acidification in System (34). Hydrogen chloride which is responsible for acidification appears due to hydrolysis of $FeCl_3$ by residual water and oxidation of chloroform by air oxygen. Therefore Fleischer's SAT-complexes are in fact the chloride complexes of protoporphyrinium dication $H_4PP^{2+}(Cl)_2$ and not sitting-a-top $FeCl_3{\cdot}H_2PP$ species. These conclusions may be extended to other analogous systems in solvents of low polarity.

Conclusions

Porphyrins are amphoteric compounds. That is why reactions of metalloporphyrins complex formation are p*H*-dependent. Depending from the p*H* of solutions they form four types of ionic species HL^-, L^{2-}, H_3L^+ and H_4L^{2+} which differ in their reactivity in metal complex formation. The porphyrins acid-basic properties are changed widely and determined the mechanism of metalloporphyrins formation. In the case of porphyrin anions metallocomplexes formed at the moment of reagent mixing, while H_2L reacts with measurable rate. Porphyrinium cations H_3L^+ and H_4L^{2+} can not be coordinated by metal ions. The dication H_4L^{2+} obtains additional stability in the presence of halogen anions (Hal^-) due to formation of complexes $H_4L^{2+}(Hal^-)$ and $H_4L^{2+}(Hal^-)_2$. Products of metal salts hydrolysis and solvents themselves may be hidden sources of hydrogen donors and Hal^- anions in nonaqueous solutions. The p*H* control of reaction systems allows to explain metalloporphyrins formation peculiarities without idea of Fleischer's SAT-complex formation.

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