**Effect of pH on Formation of Metalloporphyrins**

Vladimir B. Sheinin, a,⇑ Olga R. Simonova, a and Ekaterina L. Ratkova b

aInstitute of Solution Chemistry of Russian Academy of Science, Ivanovo, 153045, Russia.
bIvanovo State University of Chemistry and Technology, Ivanovo, 153000, Russia.

⇑Corresponding author E-mail: vbs@isc-ras.ru

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 + pH-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 pH control of reaction systems allows us to explain the peculiarities of metalloporphyrins formation without invoking the Fleischer’s idea of SAT-complexes.

**Introduction**

Substituted derivatives of 21H,23H-porphine (H2P) are named porphyrins (H3L). 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 L2–, HL–, H3L+ and H4L2+ according to Equilibria (1)-(4) which are correct for polar solvents (S):

\[
\begin{align*}
H_3L & \leftrightarrow K_{a1} H_2L + H^+ \quad (1) \\
HL^- & \leftrightarrow K_{a2} L^{2-} + H \quad (2) \\
H_2L + H^+ & \leftrightarrow K_{a3} H_3L^+ \quad (3) \\
H_3L^+ + H^+ & \leftrightarrow K_{a4} H_4L^{2+} \quad (4)
\end{align*}
\]

Due to the double positive charge and presence of four endocyclic NH-groups which are hydrogen bonds donors, the dication H4L2+ in contrast to H3L and H2L+ exhibits properties of the anion-molecular receptor [1-3]. In solutions H2L2+ exists only in the form of supramolecular homogeneous and heterogeneous complexes with solvent molecules and background anions - H2L2+S2, H2L2+S(X–) and H4L2+(X–). Equilibria (1)-(4) cover a wide pH range. Deuteroporphyrin IX dimethyl ester (H2DP) 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 H2DP 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. M2P, porphyrins can be considered as dianionic tetradeinate ligands. The reactivity of the ionic forms of porphyrins in complexation with metal cations decreases in the order \( L^{2-} > HL^- > H_2L > H_3L^+ > H_4L^{2+} > H_4L^2+(Hal^-) > H_4L^{2+}(Hal^-)_2 \). Therefore acid-base properties of porphyrins and pH of the medium should have a strong influence on the mechanism of metalloporphyrin formation.

Complexes of Cd2+ with “acidic” porphyrazine, H2PA, and its derivatives are formed in System (5) as a result of interaction between the metal ion and the most reactive form of ligand (L2–) according to Equilibrium (6): [5].

\[
\begin{align*}
\text{Cd}(	ext{Ac})_2 & \rightarrow H_2L - \text{HClO}_4 - \text{DMSO} \quad (5) \\
L^{2-} + \text{Cd}^{2+} & \leftrightarrow K_{st} \rightarrow \text{CdL} \quad (6)
\end{align*}
\]
The H2PA molecules are ionized partly even in pure DMSO ($pH \approx 10$) – the quota of $[\text{HPA}^+]$ and $[\text{PA}^{2-}]$ is $1.14$ and $4 \times 10^{-4}$ %, 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 porphyrazines are formed instantaneously upon mixing of reagents. Equilibrium (6) can be observed only in acidified solutions of DMSO when only H2L 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).

$$\text{H}_2\text{L} + \text{Cd}^{2+} \rightleftharpoons K_v \text{CdL} + 2\text{H}^+ \quad (7)$$

$$K_v = K_{st}K_{d1}K_{d2} \quad (8)$$

**Figure 1.** Equilibrium composition observed for H2PA in System (5) at 298 K.

Figure 1 shows equilibrium composition for System (5) in the case of H2PA. In the point of half-conversion the equilibrium concentration of $[\text{PA}^{2-}]$ is only $6.38 \times 10^{-25}$ M and its quota is $6.38 \times 10^{-15}$ %. 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).

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

$$V = k' [\text{M}^{2+}][\text{H}_2\text{L}] \quad (10)$$

$$k' = kK_{d1}K_{d2}/[\text{H}^+]^2 \quad (11)$$

Common porphyrins (H2P and its derivatives obtained by substitution of exocyclic hydrogen atoms), have much weaker acidic properties than porphyrazines - the difference in the $K_{st}$ values is more than 11 orders of magnitude. In this case the neutral form H2L was postulated as the reactive particle in the complex formation.\textsuperscript{[11-13]} In neutral DMSO at overall concentration of H2L $1 \times 10^{-5}$ M the equilibrium concentration of $[\text{L}^{2-}]$ is not exceeded $10^{-33}$ M. In addition, the mechanisms and conditions of formation and dissociation of common porphyrin complexes are different.\textsuperscript{[14]} Because of that complexation reaction of common porphyrins (12) proceeds slowly and irreversibly:

$$\text{H}_2\text{L} + \text{M}^{2+} \rightleftharpoons K_v \text{ML} + 2\text{H}^+ \quad (12)$$

It is assumed that positively charged protonated forms of common porphyrins H2L+ and H2L2+ can not be coordinated by metal cations.\textsuperscript{[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)\textsuperscript{[18,19]} in nonaqueous solutions. This enables the investigation of the pH influence on complexation equilibrium using electronic absorption spectroscopy. Results of the spectropotentiometric investigation 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.

$$\text{H}_2\text{MP} \rightarrow \text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O} \rightarrow \text{DMSO} \quad (13)$$

$$\text{H}_2\text{MP} \rightarrow \text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O} \rightarrow \text{HClO}_4 \rightarrow \text{DMSO} \quad (14)$$

**Experimental**

**Reagents**

Mesoporphyrin IX dimethyl ether (H2MP) was prepared according to the known method\textsuperscript{[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).\textsuperscript{[21]} Residual amount of water was 0.2267%. Chemically pure HClO4·3H2O was used without additional purification. Analytically pure Cu(NO3)2·3H2O was prepared as described elsewhere.\textsuperscript{[22]} Pure EtNCl was recrystallized twice from dry acetonitrile and dried during 24 hours under vacuum (0.01 mmHg) at room temperature. EtNClO4 was prepared as described elsewhere.\textsuperscript{[22]}
Effect of pH on Formation of Metalloporphyrins

was prepared by precipitation as result of mixing chemically pure HClO₄-3.5H₂O with purified Et₄NCl. 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)](image)

Electronic absorption spectra were measured with spectrophotometer Agilent 8453. Potentiometric measurements (accuracy 1 mV) were carried out with Element (15), using p

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 thermostat.

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 pH values of buffer solutions in DMSO in the temperature range 298 – 318 K.[18,23]

<table>
<thead>
<tr>
<th>Composition (1:1)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>picric acid + it’s lithium salt</td>
<td>0.05</td>
</tr>
<tr>
<td>salicylic acid + it’s sodium salt</td>
<td>0.05</td>
</tr>
<tr>
<td>2- nitrobenzoic acid + it’s sodium salt</td>
<td>0.05</td>
</tr>
<tr>
<td>benzoic acid + it’s sodium salt</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Kinetic Experiment

Reaction (12) was investigated in systems I, II, III, IV, V and VI (Table 3). To 75 ml of the pH-neutral or acidified H₂MP solution 3 ml of the concentrated solution of Cu(NO₃)₂·3H₂O was added and following changes of pH and electronic absorption spectra were registered.

Calculations

Values of [CuMP] and [H₂MP] were calculated using Equations (16)-(18).

\[ C_{\text{HMP}} = [\text{CuMP}] + [\text{H}_2\text{MP}] + [\text{H}_2\text{MP}^+] + [\text{H}_2\text{MP}^{2+}](\text{DMSO})_2 \]  

\[ A_T = [\text{CuMP}] + [\text{H}_2\text{MP}] + [\text{H}_2\text{MP}^+] + [\text{H}_2\text{MP}^{2+}](\text{DMSO})_2 \]  

\[ [\text{H}_2\text{MP}] = \frac{C_{\text{HMP}} - [\text{CuMP}]}{1 + K_{b1}a_{H^+}^2 + K_{b2}K_{b3}a_{H^+}^2} \]  

where \( C_{\text{HMP}} \) - general concentration of porphyrin, M; \( A_T \) - current value of optical density; \( \varepsilon \) – 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.

<table>
<thead>
<tr>
<th>System</th>
<th>(13)</th>
<th>(14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH₀</td>
<td>9.99</td>
<td>9.99</td>
</tr>
<tr>
<td>( C_{\text{HMP}}^a )</td>
<td>3.38×10⁻⁵</td>
<td>2.78×10⁻⁵</td>
</tr>
<tr>
<td>( C_{\text{Cu(NO}_3)_2\cdot3H_2O}^a )</td>
<td>2.90×10⁻²</td>
<td>1.45×10⁻²</td>
</tr>
</tbody>
</table>

* - analytical concentration in M at 298K
Results and Discussions

Solvolyis of Cu(NO₃)₂·3H₂O in DMSO

 Addition of Cu(NO₃)₂·3H₂O in pH-neutral DMSO leads to drastic decrease of pH (Figure 3).

Figure 3. Changes of pH in systems I-VI at 318 K.

Figure 4 shows the pH dependence from concentrations of Cu(NO₃)₂·3H₂O and HClO₄ which was used to determine acidity of Cu(NO₃)₂·3H₂O in DMSO. Both dependencies belong to one straight line which obeys Equation (19) with the correlation factor 0.9997.

\[ pH = -1.241 \log C + 2.91; \quad N=56 \]  

(19)

Under such experimental conditions the Cu(NO₃)₂·3H₂O is strong one-basic acid. The complex Cu⁺(OH)(DMSO)₅ is a product of the salt solvolysis. Moreover, in the case of non-hydrated copper(II) salt the complex Cu⁺(OH)(DMSO)₅ might be a product of interactions with residual water.

Protonation of H₂MP in DMSO

Protonation of H₂MP according to Equilibria (3) and (4) was investigated in System (20) at 298-318 K. [8]

\[ \text{H}_2\text{MP–HClO}_4^-\text{– DMSO} \]  

(20)

As it has been shown, the porphyrinum dication H₂MP⁺(DMSO)₂ exhibits properties of the anion molecular receptors. [1-3] In the system (20) the equilibrium (21) is completely displaced to the right side while formation of complexes with H₂O, ClO₄⁻ and NO₃⁻ are suppressed with excess of solvent.

\[ \text{H}_2\text{MP}^{2+} + 2\text{DMSO} \rightleftharpoons \text{H}_2\text{MP}^{2+}(\text{DMSO})_2 \]  

(21)

It has been shown[6] that increase of stability of the porphyrin solvatocomplex leads to levelling of \( K_{b1} \) and \( K_{b2} \) values. The value of \( \log(K_{b1}/K_{b2}) \) is equal to 0.83 for H₂MP in DMSO and to 4.44 in acetonitrile under the same conditions (at 298 K). Generally, both Equilibria (3) and (4) are overlapped at \( \log(K_{b1}/K_{b2}) < 4 \). [25] The constants of acid dissociation of H₂MP in DMSO are unknown. Value of \( pK_a1 \) for H₂MP in DMSO should be higher than that for H₂DP (\( pK_{a1} = 25.30 \) 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 pH range from −2.5 to 4.0 (Figure 5) ignoring the equilibrium concentrations of HMP⁻ and MP⁺.

Figure 5. Dependences of equilibrium concentrations from pH in System (20)

\[ C_{\text{H}_2\text{MP}} = [\text{H}_2\text{MP}] + [\text{H}_2\text{MP}^+] + [\text{H}_2\text{MP}^{2+}(\text{DMSO})_2] \]  

(22)

\[ [\text{H}_2\text{MP}] = \frac{100\%}{1 + K_{b1} \cdot a_{H^+} + K_{b1} \cdot K_{b2} \cdot a_{H^+}^2} \]  

(23)

\[ [\text{H}_2\text{MP}^+] = K_{b1} \cdot a_{H^+} \cdot [\text{H}_2\text{MP}] \]  

(24)

\[ [\text{H}_2\text{MP}^{2+}(\text{DMSO})_2] = K_{b1} \cdot K_{b2} \cdot a_{H^+}^2 \cdot [\text{H}_2\text{MP}] \]  

(25)

In Figure 5 it is possible to allocate areas corresponding individual step of Equilibrium (3) at pH > 1.7 and Equilibrium (4) at pH < −1.5, while at 1.7 > pH > −1.5 both Equilibria (3) and (4) are overlapped. In the electronic
Effect of pH on Formation of Metalloporphyrins

absorption spectra (Figure 6) the equilibria between pairs of light-absorbing species \( \text{H}_2\text{MP}, \text{H}_3\text{MP}^+, \text{H}_4\text{MP}^{2+} \); \( \text{H}_2\text{MP}^{2+}(\text{DMSO})_2 \) correspond to individual series of isobestic points at 462; 512; 612 and 558; 609 nm, respectively. The isobestic points are not observed in the area of the triple equilibrium between \( \text{H}_2\text{MP}, \text{H}_3\text{MP}^+ \) and \( \text{H}_4\text{MP}^{2+}(\text{DMSO})_2 \).

Figure 6. Changes of electronic absorption spectra in System (20) in the pH range from -2.5 to 4.0 at 318 K; (→) \( \text{H}_2\text{MP} \); (⋯) \( \text{H}_3\text{MP}^+ \).

\[ \text{Cu(NO}_3)_2\cdot3\text{H}_2\text{O} + 5\text{DMSO} \rightarrow \text{Cu}^{2+}(\text{OH})^-(\text{DMSO})_3 + 2\text{H}_2\text{O} + 2\text{NO}_3^- + \text{H}^+ \]  \hspace{1cm} (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 \( \text{H}_2\text{MP} \), which occurs only at lower values of \( \text{pH} \). 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 \( \text{H}_2\text{MP} \) and \( \text{Cu}^2+ \) (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.

\[ A = a \cdot \ln([\text{H}_2\text{MP}] + [\text{Cu}^2+]) \]  \hspace{1cm} (27)

Figure 7. Changes of electronic absorption spectra in Systems I-IV (Table 4); (→) \( \text{H}_2\text{MP} \) at pH 9.99; (⋯) \( \text{Cu}^2+ \) at pH 4.00 – 2.71.

Table 4. Parameters of reaction systems I – VI with regard to solvolysis of \( \text{Cu(NO}_3)_2\cdot3\text{H}_2\text{O} \) and protonation of \( \text{H}_2\text{MP} \)

<table>
<thead>
<tr>
<th>System</th>
<th>I (13)</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range of pH</td>
<td>9.99-3.87</td>
<td>9.99-3.87</td>
<td>9.99-4.00</td>
<td>3.01-2.71</td>
<td>1.31-1.23</td>
<td>0.61-0.60</td>
</tr>
<tr>
<td>( [\text{H}_2\text{MP}]_0 )</td>
<td>3.38×10^{-5}</td>
<td>2.78×10^{-5}</td>
<td>2.98×10^{-5}</td>
<td>2.89×10^{-5}</td>
<td>1.93×10^{-5}</td>
<td>0.69-10^{-5}</td>
</tr>
<tr>
<td>( % of ( \text{Cu}^{2+} ))</td>
<td>(100)</td>
<td>(100)</td>
<td>(100)</td>
<td>(98.91)</td>
<td>(64.01)</td>
<td>(22.75)</td>
</tr>
<tr>
<td>( C_{\text{Cu}(\text{DMSO})_3\text{OH}} )</td>
<td>2.90×10^{-2}</td>
<td>1.45×10^{-2}</td>
<td>2.90×10^{-3}</td>
<td>2.98×10^{-3}</td>
<td>2.98×10^{-3}</td>
<td>2.98×10^{-3}</td>
</tr>
<tr>
<td>( R ) (Figure 5)</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
<td>0.997</td>
</tr>
<tr>
<td>( \lg k_{e} ) (318 K)</td>
<td>-3.12</td>
<td>-3.36</td>
<td>-3.86</td>
<td>-3.86</td>
<td>-4.01</td>
<td>-4.17</td>
</tr>
</tbody>
</table>

\( \text{e} \text{ equilibrium concentration, M (at 298 K).} \)
The system IV was investigated at initial pH = 3 (beginning of protonation of H₂MP) when total equilibrium content of H₂MP⁺ and H₂MP²⁺(DMSO)₂ is 1% and the results of kinetic measurements can not be influenced. This value of pH was only one unit less then that at the end of Cu(NO₃)₂·3H₂O solvolyis. The acidification sharply narrows the interval of pH change to 0.3 units (Figure 5). As has been shown above the salt Cu²⁺H₂O(DMSO)₃ 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 H₂MP, H₂MP⁺ and H₂MP²⁺(DMSO)₂ (Figure 5) were investigated under initial conditions (Table 4). The pH changes in systems V and VI are very small.

![Figure 9. Changes of electronic absorption spectra of system VI](image)

At the constant value of pH the ratio of components in the equilibrium mixture H₂MP, H₂MP⁺ and H₂MP²⁺(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 character of the ligand is H₂MP. In systems I – III the formation of CuMP was studied at various excesses of salt and constant H₂MP concentration. In systems IV, V and VI it was studied at constant concentration of Cu(NO₃)₂·3H₂O 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 H₂MP. The dependences of effective constant of Reaction (29) from the concentration of the salt Cu(NO₃)₂·3H₂O (in Systems I-IV) and on the concentration of H₂MP (in Systems IV-VI) were obtained. In the case of the first order in salt, effective kₑ and true kₑ constants can be connected by linear Equation (30). It was experimentally confirmed that this equation is correct for all investigated Systems I-VI.

\[
\begin{align*}
\text{Cu}^{2+} & (\text{OH})^+ (\text{DMSO})_3 + \text{H}_2\text{MP} \\
& \rightarrow \text{CuMP} + \text{H}_2\text{O} + \text{H}^+ + 5\text{DMSO} \\
k_{\text{ef}} & = k_e [\text{H}_2\text{MP}][\text{Cu}^{2+} (\text{OH}) (\text{DMSO})_3] \\
\end{align*}
\]

The experimental dependence of \( k_{\text{ef}} \) from [H₂MP][Cu²⁺(OH)(DMSO)₃] (Equation (31)) have the correlation coefficient \( R = 0.9998 \) (Figure 10).

\[
k_{\text{ef}} = (884.66 \pm 9.47)[\text{H}_2\text{MP}][\text{Cu}^{2+}(\text{OH})(\text{DMSO})_3] \quad (31)
\]

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

![Figure 10. Correlation between \( k_{\text{ef}} \) and [H₂MP][Cu²⁺(OH)(DMSO)₃] for Reaction (29) in Systems I–VI at 318 K.](image)

**Fleischer’s SAT-complex**

The porphyrinium dications H₄L²⁺ have properties of pH-dependent anion-molecular receptors. They are formed due to sequential protonation coordination cavity of porphyrin macrocycle by two proton. The second proton activates porphyrin receptor H₄L²⁺ and starts up self-assembling of anion-molecular complexes H₄L²⁺S₂, H₄L²⁺SB and H₄L²⁺B₂ (B – molecular or anion substrate). The composition and stability of these complexes are determined by each reaction system.

\[
\begin{align*}
\text{H}_4\text{L}^{2+} & \cdot \text{S}_2 + \text{B} \underset{k_{d1}}{\overset{k_{d1}}{\rightleftharpoons}} \text{H}_4\text{L}^{2+} \cdot \text{SB} + \text{S} \\
\text{H}_4\text{L}^{2+} & \cdot \text{SB} + \text{B} \underset{k_{d2}}{\overset{k_{d2}}{\rightleftharpoons}} \text{H}_4\text{L}^{2+} \cdot \text{B}_2 + \text{S}
\end{align*}
\]

Generally, values of \( K_{d1}, K_{d2}, K_{a1}, K_{a2} \) exhibit antibatic dependencies from basicity (DN) and polarity (e) of solvents In highly basic and polar DMSO (reaction System (14)) the dication H₄L²⁺ exists as molecular complex H₄L²⁺(DMSO)₂. Because of small values of \( K_{d1} \) and \( K_{d2} \) (Table 1), large excess of acid is necessary for formation of H₄L²⁺ in DMSO. The values of \( K_{d1} \) and \( K_{d2} \) are increased by ten and seven of orders magnitude in going from DMSO to moderately basic and polar acetonitrile (AN). The dication H₄L²⁺ is characterized by high selectivity to halide-ions. As it can be seen (Table 5), the complexes H₄L²⁺(AN)(Hal⁻) and H₄L²⁺(Hal⁻)₂ are very stable. Due to the formation of H₄L²⁺(CT)₂ in acetonitrile the energy of stabilization of H₄L²⁺ achieves 54.4 kJ/mol.
Effect of pH on Formation of Metalloporphyrins

Table 5. Constants of Equilibriums (32) and (33) in system H₂MP – HClO₄ – B – acetonitrile at 298 K

<table>
<thead>
<tr>
<th>( \text{Substrate (B)} )</th>
<th>( \text{ClO}_4^- )</th>
<th>( \text{H}_2\text{O} )</th>
<th>( \text{I}^- )</th>
<th>( \text{Br}^- )</th>
<th>( \text{Cl}^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{PP} ) – FeCl₃ – CHCl₃</td>
<td>( \text{H}_2\text{PP}^{2+} )(A)(Hal), ( \text{H}_2\text{PP}^{2+} )(Hal)² and ( \text{H}_2\text{PP}^{2+} )(AN)₂</td>
<td>(&lt;1)</td>
<td>(0.93±0.08)</td>
<td>(4.27±0.02)</td>
<td>(5.13±0.01)</td>
</tr>
<tr>
<td>( \text{H}_2\text{PP} ) – FeCl₃ – CHCl₃</td>
<td>( \text{H}_2\text{PP}^{2+} )(A)(Hal), ( \text{H}_2\text{PP}^{2+} )(Hal)² and ( \text{H}_2\text{PP}^{2+} )(AN)₂</td>
<td>(&lt;1)</td>
<td>(0.52±0.05)</td>
<td>(2.83±0.01)</td>
<td>(3.31±0.03)</td>
</tr>
</tbody>
</table>

Complexes \( \text{H}_2\text{MP}^{2+} \)(AN)(Hal), \( \text{H}_2\text{MP}^{2+} \)(Hal)² and \( \text{H}_2\text{MP}^{2+} \)(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 [20] in a new way.

In this system instead of the Fe³⁺ complex ClFe³⁺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 \( \text{H}_2\text{PP}^{2+} \).

Addition of such bases as pyridine and ethanol destroys the SAT-complex with appearance of the molecular form \( \text{H}_2\text{PP}^{2+} \).

This SAT-complex was considered as a mixed complex FeCl₃H₂PP. This conclusion did not take into account self-acidification in System (34). Hydrogen chloride which is responsible for acidification appears due to hydrolysis of FeCl₃ by residual water and oxidation of chloroform by air oxygen. Therefore Fleischer’s SAT-complexes are in fact the chloride complexes of protoporphyrinium dication \( \text{H}_2\text{PP}^{2+}(\text{Cl})_2 \) and not sitting-a-top FeCl₃-H₂PP 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 pH-dependent. Depending on the pH of solutions they form four types of ionic species H₂L⁺, L₂⁺, H₂L⁻ and H₂L²⁻ 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 H₂L reacts with measurable rate. Porphyrinium cations H₂L⁺ and H₂L²⁻ can not be coordinated by metal ions. The dication H₂L²⁺ obtains additional stability in the presence of halogen anions (Hal⁻) due to formation of complexes H₂L²⁺(Hal⁻) and H₂L²⁺(Hal)². Products of metal salts hydrolysis and solvents themselves may be hidden sources of hydrogen donors and Hal⁻ anions in nonaqueous solutions. The pH control of reaction systems allows to explain metalloporphyrins formation peculiarities without idea of Fleischer’s SAT-complex formation.

References