Complexation of 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrin with Zinc(II) Ions in Aqueous Solution

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The protonation equilibria of tetrakis(4-sulfonatophenyl)porphyrin sodium salt, $Na_4[H_2tpps]$, and its complex formation with Zn^{2+} ion in aqueous solutions were studied over a wide range of pH values, (2 to 12), using a combination of spectrophotometric and potentiometric methods at constant temperature, 25 °C, and constant ionic strength (0.1 $mol \cdot dm^{-3}$ sodium perchlorate). Least squares regression calculations are consistent with the formation of $Zn(H_2O)_2L$, $Zn(H_2O)(OH)L$, and $Zn(OH)_2L$, species, where L represents $tpps^{6-}$. The hydrolysis of zinc ion was also investigated spectrophotometrically in aqueous solution and four hydrolytic species were specified in the mentioned experimental conditions. Finally, the species mole fraction of the hydrolyzed and the complex species were plotted at different pH values and discussed.

Introduction

Metalloporphyrins are examples of macrocyclic complexes and have been extensively studied from several viewpoints.[1] The important biological roles of porphyrins in the living cell as well as their clinical and industrial potential have attracted increasing interest. The elucidation of the mechanisms involved in porphyrin complexation reactions is among the processes most extensively studied over the past several years.[2–8] Most of these reports are limited to low pH conditions to avoid formation of polyoxometal complexes.

The equilibrium between a divalent metal ion and a free base porphyrin, H_2tpps^{4-}, to form a metalloporphyrin (MP) is usually represented by the equation

$$M^{2+} + H_2P \rightleftarrows MP + 2H^+ \quad (1)$$

So far, some works have been devoted to the study of formation constants of Zn^{2+} with different porphyrins because of their relevance in biological systems.[9–13] However, the formation equilibria of the complexes have been mostly determined from kinetic data or have been studied in only one or a few wavelengths without consideration of the variation of pH during the formation reactions and missing the oxometal complex species which are important in aqueous solutions. These studies were mostly performed using the spectrophotometric method, and the results indicate formation of only one complex species, ZnP, with a large difference in the calculated formation constants.[10–13] However, we believe that increasing the pH of solution, from acidic to alkali, causes deprotonation of water molecules bound to the Zn^{2+}−porphyrin and results in the formation of mixed hydroxo complex species with their concentrations depending on the pH of the solution.

The present work is concerned with the study of protonation equilibria of tetrakis(4-sulfonatophenyl)porphyrin, (H_2tpps^{4-}), as well as the formation equilibria of the complex species $[Zn(H_2O)_2tpps]^{4-}$, $[Zn(H_2O)(OH)tpps]^{5-}$, and $[Zn(OH)_2tpps]^{6-}$ in aqueous solution over a wide pH range, (2 to 12). The main difficulties in determining the formation equilibria of metalloporphyrins are the very low rates of the reactions at room temperature and the limited solubility of the porphyrins as well as the interference of other equilibria caused by hydrolysis of the metal ions.

Experimental Section

Chemicals. Tetrakis(4-sulfonatophenyl)porphyrin sodium salt, $Na_4[H_2tpps]$, was synthesized by the method described before.[14] Zinc(II) nitrate was obtained from Merck (reagent grade) and was used without further purification. Sodium perchlorate was from Merck and was dried under vacuum at room temperature for at least 48 h before use. NaOH solution was prepared from a titrisol solution (Merck), and its concentration was determined by several titrations with a standard HCl solution. Perchloric acid was from Merck and was used as supplied. All dilute solutions were prepared from double-distilled water with a conductivity equal to (1.3 ± 0.1) $\mu S \cdot cm^{-1}$.

To determine the purity of the synthesized porphyrin, the absorption coefficient of H_2tpps^{4-} was measured at different pH values. The absorption coefficient was calculated and compared with the value in the literature.[14]

Measurements. All measurements were carried out at 25 °C. The ionic strength was maintained at 0.1 $mol \cdot dm^{-3}$ with sodium perchlorate. A Jenway research pH-meter, model 3520, was used for the pH measurements. The hydrogen ion concentration was measured with a combination electrode. The pH-meter was calibrated for the relevant H^+ concentration with a solution of 0.01 $mol \cdot dm^{-3}$ perchloric acid containing 0.09 $mol \cdot dm^{-3}$ sodium perchlorate (for adjusting the ionic strength to 0.1 $mol \cdot dm^{-3}$). For this standard solution, we set $-\log[H^+] = 2.00$.[15] Junction potential corrections are calculated from eq 2

$$-\log[H^+]_{real} = -\log[H^+]_{measured} + a + b[H^+]_{measured} \quad (2)$$

Here a and b were determined by measuring of hydrogen ion concentration for different solutions of $HClO_4$ or NaOH with sufficient $NaClO_4$ to adjust the ionic media.

Spectrophotometric measurements were performed on a UV–vis Shimadzu 2100 spectrophotometer with a Pentium 4 computer and using thermostatted matched 10 mm quartz cells. The measurement cell was of flow type. A Masterflex pump

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Table 1. Average Values of Protonation Constants of H_2tpps^{4-} at 25 °C and Constant Ionic Strength (0.1 mol·dm^{-3} $NaClO_4$), K_1 and K_2, Assigned for the Equilibria $H_2tpps^{4-} + H^+ \rightleftarrows H_3tpps^{3-}$ and $H_3tpps^{3-} + H^+ \rightleftarrows H_4tpps^{2-}$, Respectively

log K_1	log K_2	ref
4.854 ± 0.002	4.913 ± 0.003	this work
4.76	4.99	24
4.86	4.95	25
4.60	5.17	26
4.80		27

allowed circulation of the solution under study from the potentiometric cell to the spectrophotometric cell, so the absorbance and $-\log[H^+]$ of the solution could be measured simultaneously. To exclude carbon dioxide from the system, a stream of purified nitrogen was passed through a sodium chloride solution and then bubbled slowly through the reaction solution. In all cases, the procedure was repeated at least three times and the resulting average values and corresponding deviations from the average are shown in the text and tables.

Stepwise Acidity Constants of H_2tpps^{4-}. Various anionic porphyrins tend to stack in aqueous solutions to form dimers or higher aggregates in concentrated aqueous solutions. The equilibrium constants for dimerization have been reported to be 10^4 to 10^7 for several water soluble porphyrins.[16–20] Deviations from Beer's law are often used to investigate the porphyrin aggregation in solution. The UV–vis absorption spectra of H_2tpps^{4-} at 25 °C and ionic strength 0.1 mol·dm^{-3} sodium perchlorate at several pH values were measured at different concentrations ((1.5·10^{-5} to 2.5·10^{-5}) mol·dm^{-3}). Beer's law held quite well, indicating that no aggregation of the porphyrin occurs under our experimental conditions.

A 50 mL acidic solution, 0.1 mol·dm^{-3} $HClO_4$, of H_2tpps^{4-}, 2.59·10^{-6} mol·dm^{-3}, was titrated with an alkali solution, 0.1 mol·dm^{-3} NaOH, both of the same ionic strength, 0.1 mol·dm^{-3}. The $-\log[H^+]$ and absorbances, (200 to 800) nm, were measured after the addition of a few drops of titrant, and the procedure was continued up to the required pH, 12.

Complexation of Zn^{2+} by H_2tpps^{4-}. Considering that the formation reaction rate of metalloporphyrins is very slow, evolution of the absorption spectra should be carefully followed over a long time to be sure that equilibrium is achieved. To overcome this problem, we have prepared 250 mL of an acidic stock solution, 0.1 mol·dm^{-3}, of Zn^{2+}, 6.66·10^{-6} mol·dm^{-3}, which is thermostatted at 25 °C. Into each of 50 10 mL volumetric flasks was placed 4 mL of the above solution. An alkali, 0.1 mol·dm^{-3}, solution of porphyrin, 7.74·10^{-6} mol·dm^{-3}, was added to the respective flasks in the order: (1.0, 1.1, 1.2, . . ., and 5.0) mL, This was followed by adding sufficient sodium perchlorate solution, 1.0 mol·dm^{-3}, to achieve a constant ionic strength of 0.1 mol·dm^{-3}. The solutions were allowed to attain equilibrium over 24 h in the dark. During this time, they were thermostatted and agitated at 25 °C. The pH and UV–vis spectra of each solution were recorded versus wavelength, (200 to 800) nm, at 25 °C.

Results and Discussion

Acidity Constants. The determination of the acidity constants of H_2tpps^{4-} is based on the relation $A = f(\mathrm{pH})$.[21] The measured absorbance, A ((200 to 800) nm with an interval of 2 nm), and $-\log[H^+]$ from the spectrophotometric titration were input to the computer program, Squad.[22,23] The program allows calculation of the different acidity constants which are listed in Table 1. The solution is stable, and the absorption values did not change with time. The given acidity constants agree well, as far as available information goes, with those reported in the literature.[24–27]

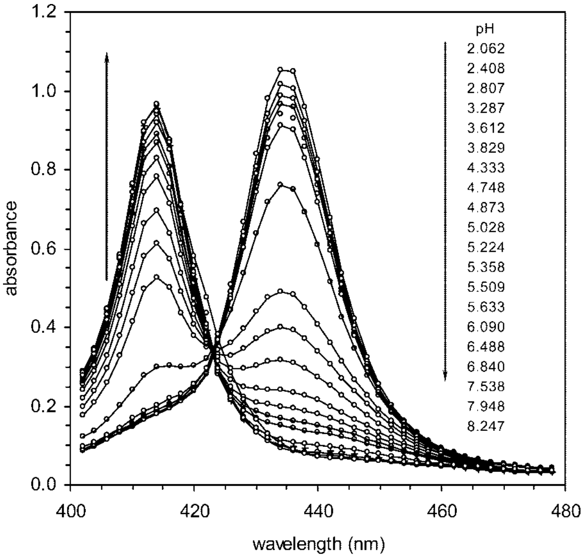

Figure 1. Visible absorption spectra of a series of aqueous solutions of H_2tpps^{4-} (2.59·10^{-6} mol·dm^{-3}) at 25 °C and different pH values.

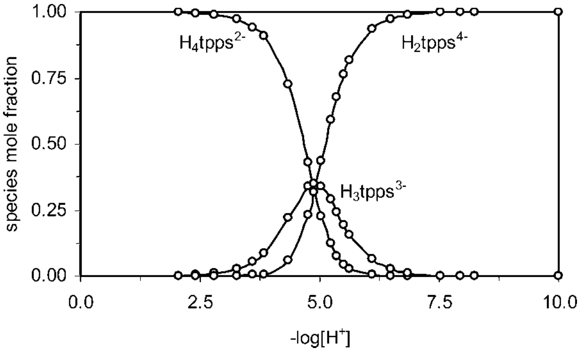

Figure 2. Distribution diagram of different protonated species of the ligand at 25 °C and 0.1 mol·dm^{-3} sodium perchlorate.

When an alkali solution was added to the acidic solution of H_2tpps^{4-}, the green color changed to purple, pH > 3, and the absorption spectrum shifted to lower wavelength with an important modification. The soret band is shifted to 415 nm where the absorption band at 435 nm progressively decreases to a lower value at pH 12 (see Figure 1).

In Figure 2, the equilibrium distribution of various species of the porphyrin is plotted as a function of $-\log[H^+]$. It is shown that the first deprotonation of the ligand occurred around pH (4 to 6) ($H_4tpps^{2-} \rightleftarrows H_3tpps^{3-} + H^+$), and the second deprotonation ($H_3tpps^{3-} \rightleftarrows H_2tpps^{2-} + H^+$) happened immediately after the first and very close to it. This process has been extensively studied by several researchers, and some have demonstrated that the two deprotonation reactions are so close to each other that both of them could be assigned only as one reaction equilibrium.[28–30] In a similar study, Baker et al. have shown[4] that problems arise when only the Soret bands are considered. For example, H_2TPyP (tetrapyridyl porphyrin) and H_2TMPyP [tetra(*n*-methyl-4-pyridyl)porphyrin] apparently have a single isobestic point in the soret, which indicates that only PH_2 and PH_4^{2+} are present in appreciable concentrations. However, an examination of the corresponding visible region clearly shows the lack of pH independent isobestic points and the monocation appears. To make this clear, we applied the computer program in two ways: calculating only one protonation

Table 2. Average Values of Hydrolysis Constants of Zn^{2+} Species [$Zn(OH)^+$, $Zn(OH)_2$, $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$, Respectively] in Aqueous Solution at Constant Ionic Strength (0.1 mol·dm^{-3} Sodium Perchlorate) and 25 °C Together with the Values Reported in the Literature

$-\log K_{Zn(OH)^+}$	$-\log K_{Zn(OH)_2}$	$-\log K_{Zn(OH)_3^-}$	$-\log K_{Zn(OH)_4^{2-}}$	ref
6.127 ± 0.003	10.367 ± 0.002	11.291 ± 0.002	11.827 ± 0.005	this work
9.00	10.00	10.3		31
8.75	9.10	10.27		32
8.77	10.26	9.10		33
		10.13	12.01	34
7.45	9.44	11.48	12.81	35
8.96	7.94	11.50	12.80	36
7.83	10.09	9.81	12.78	37

and second calculating two protonation equilibria. However, the sum of the squares errors for the first assumption is about 10 times more than that for the second one. It is also interesting to note that log *K* with the first method is very close to log K_2 in the second method (log $K = 4.89$). Finally, with another isobestic point observed at 580 nm in the visible spectrum which was pH dependent, we concluded that the monoprotonated species was formed but not in considerable concentration in the solution (Figure 2).

Hydrolysis of Zinc Ion. The hydrolysis of Zn^{2+} has been investigated at different temperatures and various pressures by several authors.[31–37] On the basis of the solubility method, some authors have detected two or three hydrolytic species,[31–34] [$Zn(OH)^+$], [$Zn(OH)_2$], and [$Zn(OH)_3$]$^-$, and some others have proposed the formation of four hydrolyzed species, [$Zn(OH)$]$^+$, [$Zn(OH)_2$], [$Zn(OH)_3$]$^-$, and [$Zn(OH)_4$]$^{2-}$, with some differences between the calculated hydrolysis constant values.[35–37] Our results in this work are consistent with the formation of four mononuclear hydrolytic species of Zn^{2+}. The hydrolysis constant, K_{hyd}, in general is defined as

$$Zn^{2+} + nH_2O \rightleftarrows Zn(OH)_n{}^{2-n} + nH^+ \qquad (3)$$

$$K_{hyd} = [Zn(OH)_n{}^{2-n}][H^+]^n/[Zn^{2+}] \qquad (4)$$

where $n = 1$, 2, 3, and 4.

The method of determination of K_{hyd} is based on the relation $A = f(pH)$. Absorbance, *A*, and $-\log[H^+]$ were measured for a solution of Zn^{2+} with sufficient NaOH solution. Treatment of the spectrophotometric data ((200 to 500) nm with an interval of 2 nm) obtained during the titrations as a function of hydrogen ion concentration was submitted to the computer program, Squad. Using the autoprotolysis constant of water (calculated at 25 °C and 0.1 mol·dm^{-3} sodium perchlorate as $pK_W = 13.76$), the data were fitted to eq 3 to determine the hydrolysis constants for different species, and the selected values are listed in Table 2 with the values reported before.

With some differences, the hydrolysis constant values resulting in this work are in agreement with those reported before. The differences are possibly due to the different experimental method and the fact that a background electrolyte has been employed to determine the various species of zinc ion concentration and to maintain the ionic strength, respectively.

The species mole fraction of the observed hydrolyzed species versus $-\log[H^+]$ are plotted in Figure 3. In the figure, the first hydrolyzed species $Zn(OH)^+$ is the predominant species at pH $\cong 8$ (around 99 %), and the fourth species $Zn(OH)_4{}^{2-}$ becomes predominant at pH > 12 (around (90 to 95) %). However, the second and the third species, $Zn(OH)_2$ and $Zn(OH)_3{}^-$, are formed in lower percentages (around 50 %) at pH 10.5 and 11.5, respectively.

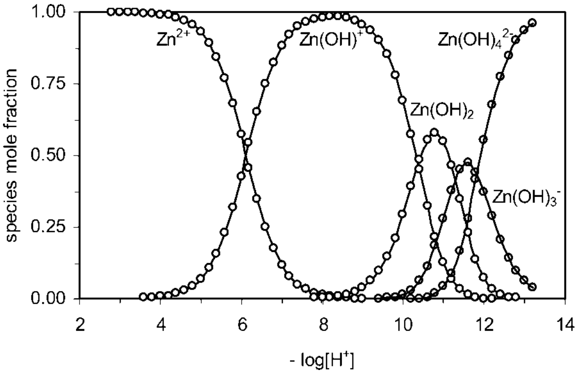

Figure 3. Distribution diagram of hydrolytic species of zinc ion versus hydrogen ion concentration at 25 °C and constant ionic strength (0.1 mol·dm^{-3} $NaClO_4$).

Complexation of H_2tpps^{4-} by Zinc Ion. The complex $M_xH_yL_z{}^{(2x+y-4z)}$ that formed is characterized by its stoichiometry (*x*:*y*:*z*), where M and L represent the metal ion and H_2tpps^{4-}, respectively. To determine the formation constant of the complexation, eq 6 is defined by K_{xyz}:

$$xM^{2+} + yH^+ + zL^{4-} \rightleftarrows M_xH_yL_z{}^{(2x+y-4z)} \qquad (5)$$

$$K_{xyz} = [M_xH_yL_z]/([M^{2+}]^x[H^+]^y[L^{4-}]^z) \qquad (6)$$

Determination of the formation constant was employed using the method mentioned before. Absorbance, *A*, and $-\log[H^+]$ were measured by successive addition of an alkali solution of the ligand to the metal ion solution; see the Experimental Section. Treatment of the spectrophotometric data (every 2 nm) obtained during the titrations, as a function of the H^+ concentration, were conducted with the computer program.

The stoichiometric formation constants were computed from the data using the computer program Squad. The number of experimental points (absorbance versus pH) was more than 30 (maximum 40) for each titration. If we designate *m* absorption spectra that will be measured at *n* wavelengths, the individual absorbance readings thus can be arranged in an $m \times n$ matrix **R**; the *m* spectra form the rows of **R**, and the columns consist of the *n* response curves gathered at the different wavelengths. According to Beer's law, for a system with *N* absorbing components, **R** can be decomposed into the product of a concentration matrix **C** ($m \times N$) and a matrix of the molar absorptivities **S** ($N \times n$). However, because of the inherent noise in the measured data, the decomposition does not represent **R** exactly. The matrix **T** of the residuals is given by the difference between **CS** and **R**

$$\mathbf{T} = \mathbf{CS} - \mathbf{R} \qquad (7)$$

In the fitting procedure, those matrices **C** and **S** are determined which best represent the original matrix **R**. The task of the fitting procedure is to optimize the matrix **T** of the residuals, eq 7, according to the least-squares criterion. In eq 8, *U* is the sum of the squares of all elements of **T**. It is the task of the nonlinear least-squares fitting to find the set of parameters that result in a minimum of *U*.

$$U = \sum_{i=1}^{m} \sum_{j=1}^{n} T(i,j)^2 = \text{minimize} \qquad (8)$$

In a donor solvent like water, zinc(II)−porphyrin possibly exhibits a preference for a six-coordinated structure[38] which is similar to that of iron(III)−porphyrins.[39] The X-ray crystallographic and molecular studies of Zn(II)−porphyrin (5,10,15,20-

Table 3. Average Values of Formation Constants of the Zinc−Porphyrin System ($Zntpps^{4-}$, $ZnH_{-1}tpps^{5-}$, and $ZnH_{-2}tpps^{6-}$, respectively) at 25 °C and Constant Ionic Strength (0.1 $mol \cdot dm^{-3}$ $NaClO_4$) Together with Values Reported in the Literature

$-\log K_{Zn-tpps^{4-}}$	$-\log K_{Zn-H_{-1}tpps^{5-}}$	$-\log K_{Zn-H_{-2}tpps^{6-}}$	ref
3.474 ± 0.004	5.777 ± 0.002	6.862 ± 0.003	this work
1.84			10
0.43			13

tetraphenyl porphyrin) have revealed the capability of the zinc ion to bind with two molecules of solvents in the axial position and occupy a position in the mean plane of the porphyrin ligand.[38] Further, a kinetic study has been performed on the reaction of Cr(III) with meso-tetrakis(*p*-sulfonatophenyl)porphyrin in aqueous solution to characterize the presence of solvent molecules in the formed complex species.[40] The authors have concluded that by increasing the pH of solution from 6 to 10, the formation of $Cr{-}tpps(H_2O)_2^{3-}$, $Cr{-}tpps(OH)(H_2O)^{4-}$, and $Cr{-}tpps(OH)_2^{5-}$ will occur, respectively, which is consistent with the result obtained in this work. However, different models including $M(H_2O)_2L$, $M(H_2O)(OH)L$, $M(OH)_2L$, and several polynuclear and protonated species were tested by the program. As expected, polynuclear complexes were systematically rejected by the computer program, as also were MH_2L_2, MHL_2, and ML_2 (charges are omitted for simplicity). A value for the MHL species was also calculated by the program, but the species was not considered further, because the estimated error in its formation constant was not acceptable and its inclusion does not improve the goodness of the fit. The models finally chosen, formed by $M(H_2O)_2L$, $M(H_2O)(OH)L$, and $M(OH)_2L$, besides the hydrolysis products of the zinc ion resulted in a satisfactory numerical and graphical fitting, which are listed in Table 3 together with the values reported before.[10–13]

To verify the formation of hydroxo complex species in solution, we again applied the computer program in two ways: taking into account only $ML(H_2O)_2$ or taking into account $ML(H_2O)_2$, $ML(H_2O)(OH)$, and $ML(OH)_2$ species (charges are omitted for simplicity). However, the sum of the squares errors for the first assumption is about 25 times more than the second one. This finding and those mentioned before rule out the formation of ML species alone. Interestingly, the formation constant value computed in the first way is 0.31 which is very close to the value reported previously.[13]

In Figure 4, the spectrophotometric titrations curves are presented for the complexes of H_2tpps^{4-} with Zn^{2+} and also the different species of H_2tpps^{4-} alone at various wavelengths.

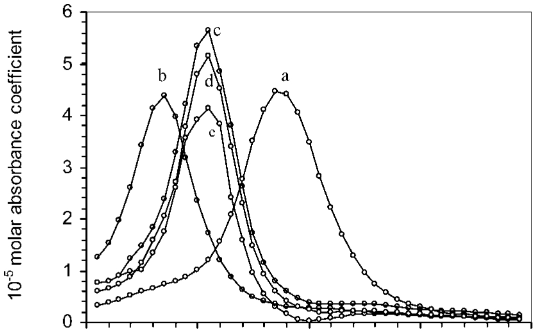

Figure 4. Molar absorption coefficient of a series of aqueous solutions of the H_2tpps^{4-} ($2.59 \cdot 10^{-6}$ $mol \cdot dm^{-3}$) and Zn^{2+} ($6.66 \cdot 10^{-6}$ $mol \cdot dm^{-3}$) system at 25 °C and ionic strength of 0.1 $mol \cdot dm^{-3}$ ($NaClO_4$): (a) H_4tpps^{2-}, (b) H_2tpps^{4-}, (c) $Zntpps^{4-}$, (d) $ZnH_{-2}tpps^{4-}$, and (e) $ZnH_{-1}tpps^{4-}$.

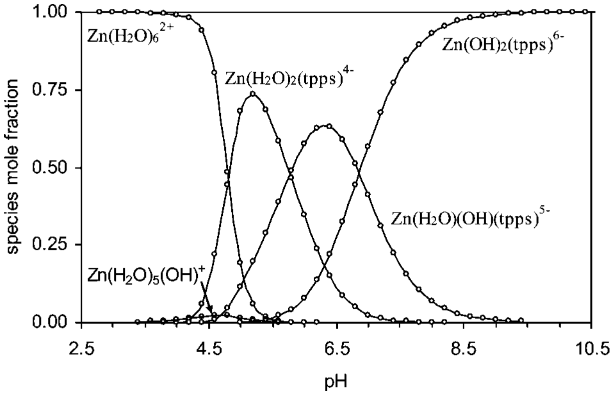

Figure 5. Distribution diagram of complex species of zinc ion ($6.66 \cdot 10^{-6}$ $mol \cdot dm^{-3}$) and H_2tpps^{4-} ($7.74 \cdot 10^{-6}$ $mol \cdot dm^{-3}$) at different pH, 25 °C, and constant ionic strength (0.1 $mol \cdot dm^{-3}$ $NaClO_4$).

Deprotonation of the ligand has been shown to induce dramatic change in the molar absorption coefficients from curves a to b and for the complex species that are designated as c, d, and e. Curve a, Figure 4, is shown for H_4tpps^{2-}; at a higher concentration of sodium hydroxide, deprotonation has occurred, and the curve undergoes a large shift to b. In the presence of the zinc ion, only one curve can be seen, c, and at higher pH, c moves to e and finally to d. The latter curves designated for the complex species $[Zn(H_2O)_2tpps]^{4-}$ (c), $[Zn(H_2O)(OH)tpps]^{5-}$ (e), and $[Zn(OH)_2tpps]^{6-}$ (d), respectively. In a kinetic study, a similar result has been found by Inamo et al.[13] without calculation of formation constants or any more attention to them. They have concluded that the hydroxocomplex species would be formed at higher pH values.

Figure 5 shows the equilibrium distribution of different species in terms of mole fractions of the $Zn^{2+}{-}H_2tpps^{4-}$ system as a function of $-\log[H^+]$. The calculation is based on the formation constant values given in Table 3. Evaluation of the titration curves for the studied system shows that the first hydrolyzed species, $Zn(OH)^+$, begins to form at pH ∼ 4. At this pH, the mole ratio of the ligand to metal ion is 0.34. The concentration of ligand is increasing with a continuing titration of the acidic metal ion with the alkali solution of the ligand that causes a decrease in the zinc ion in solution due to the formation of complex species which possess higher formation constants. The mole ratios of the ligand to metal ion are 4.78 and $4.79 \cdot 10^3$ at pH ∼ 6 and 8, respectively. So, an interruption in formation of hydrolytic species of zinc ion alone will occur when the mole ratio of the ligand to metal ion exceeds 0.34. Considering this figure, the highest concentration of the complex species $[Zn(H_2O)_2tpps]^{4-}$, $[Zn(H_2O)(OH)tpps]^{5-}$, and $[Zn(OH)_2 tpps]^{6-}$ are obtained at pH 5.2, 6.2, and 8.5, respectively.

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