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Complexation of 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrin with the Cadmium(II) Ion at Different Ionic Strengths

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The protonation equilibria of tetrakis(4-sulfonatophenyl)porphyrin sodium salt, $Na_4(H_2tpps)$, and its complex formation with the Cd^{2+} ion at different ionic strengths [(0.1 to 1.0) $mol\cdot dm^{-3}$ $NaClO_4$] were studied over a wide pH range (2 to 12) using a combination of potentiometric and spectrophotometric methods at 25 °C. Least squares regression calculations are consistent with the formation of the $Cd-Htpps^{3-}$ and $Cd-tpps^{4-}$ species. The hydrolysis of cadmium ion was also investigated specrophotometrically at different ionic strengths of sodium perchlorate, and four hydrolytic species were specified in the experimental conditions. The dependence of protonation, hydrolysis, and the formation constants of the porphyrin and the metal ion on ionic strength is described by a Debye−Hückel-type equation, and the results have been compared with data previously reported and interpreted.

Introduction

Metalloporphyrins are examples of macrocyclic complexes and have been studied extensively because of their importance in biological systems.[1−4] In recent years, several papers have been published on the mechanism and kinetics of the incorporation of some metal ions into the porphyrin nucleus.[5−12] The kinetic study of porphyrin metalation is indispensable in order to understand in vivo metal incorporation processes leading to the formation of natural metalloporphyrins. Generally, porphyrins are synthesized in a metal-free form and metal ions are subsequently inserted in the processes catalyzed by enzymes.[13] Synthetic metalloporphyrins are suitable sensitizers for photodynamic cancer therapy.[14]

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

$$M^2 + H_2P \rightleftarrows MP + 2H^+ \tag{1}$$

So far, some work has been devoted to the study of formation constants of Cd^{2+} with different porphyrins because of their relevance in biological systems.[6,7,15] However, the formation equilibria of the complexes have been mostly determined from kinetic data or have been studied at only one or a few wavelengths without consideration of the variation of pH during the formation reactions and missing the possibility of 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, CdP, with a large difference in the calculated formation constants. However, we believe that increasing the pH of solution, from acidic to alkali, possibly causes different complex species to form. There is also the possibility of deprotonation of water molecules bound to the metal ion−porphyrin, resulting in the formation of mixed hydroxo complex species with their concentrations depending on the pH of the solution. In a previous paper,[16] we described the procedure in the $Zn^{2+}-tpps$ system, but the cadmium cation is larger than the zinc cation and possibly cannot quite fit in the porphyrin ring, so it may possibly locate in the upper or lower part of the ring's plane, which may lead to less stable complex species. However, the main difficulties in determining formation equilibria of metal cation−porphyrin systems 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 the hydrolysis of the metal ions.

Regarding the ionic strength dependence of formation constants for some complexes of amino acids by some metal ions, we have recently reported some interesting features of the function $\log K = f(I)$,[17−21] where K and I refer to the formation constant and ionic strength, respectively. In particular, all the formation constants seem to follow the same trend as a function of ionic strength, if allowance is made for different types of reaction stoichiometry and different charges of reactants and products. In determining a formation constant at a fixed ionic strength, in all cases, some uncertainties are always present. This fact is mainly due to the uncertainties in numerical values of the formation constants. For example, the 0.45 log unit difference in the formation constants determined at (0.5 and 1.0) $mol\cdot dm^{-3}$ should be the result of the uncertainties in the numerical values.

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 $Cd^{2+}-tpps$ system in an ionic strength range of (0.1 to 1.0) $mol\cdot dm^{-3}$ sodium perchlorate over a wide pH range (2 to 12). The parameters that define this dependency were analyzed with the aim of obtaining further information with regard to their variation as a function of the charges involved in the complex reaction. Moreover, a Debye−Hückel-type equation was established for the dependence of the formation constant on ionic strength. This equation gives the possibility of estimating a formation constant at a fixed

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ionic strength when its value is known for another ionic strength in the range ($0.1 < I < 1.0$) mol·dm^{-3} and, therefore, may give a significant contribution to solving many analytical and speciation problems.

Experimental Section

Chemicals. Tetrakis(4-sulfonatophenyl)porphyrin sodium salt, $Na_4(H_2tpps)$, was synthesized by the method described before.[22] Cadmium(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 72 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 specific conductance equal to (1.3 ± 0.1) μS·cm^{-1}.

To determine the purity of the synthesized porphyrin the absorption coefficient of H_2tpps^{4-} was measured at different pH. The absorption coefficient was calculated and compared with the value in the literature.[22]

Measurements. All measurements were carried out at 25 °C. The ionic strength was maintained at the desired ionic strength using sodium perchlorate/perchloric acid. A Jenway research pH-meter (model 3520) was used for the pH measurements. The hydrogen ion concentration was measured with a Jenway combination electrode. The pH-meter was calibrated for the relevant H^+ concentration with a solution of 0.01 mol·dm^{-3} perchloric acid containing 0.09 mol·dm^{-3} sodium perchlorate (to adjust the ionic strength to 0.1 mol·dm^{-3}). The same procedure was performed for the other ionic strengths. For this standard solution, we set $-\log[H^+] = 2.00$.[23] Junction potential corrections were calculated from eq 2

$$-\log[H^+]_{\text{real}} = -\log[H^+]_{\text{measured}} + a + b[H^+]_{\text{measured}} \tag{2}$$

where a and b were determined by measuring of the 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 using thermostated, matched, 10 mm quartz cells. The measurement cell was of flow type. A Masterflex pump 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 hydroxide 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.

Results and Discussion

The 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.[24,25] Deviations from Beer's law are often used to investigate the porphyrin aggregation in solution. 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 [($1.5\cdot10^{-5}$ to $2.5\cdot10^{-5}$) mol·dm^{-3}]. Beer's law held quite well, indicating that no aggregation of the porphyrin occurs under our experimental conditions.

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 $H_2tpps^{4-} + H^+ \rightleftharpoons H_3tpps^{3-}$ and $H_3tpps^{3-} + H^+ \rightleftharpoons H_4tpps^{2-}$, respectively

I / mol·dm^{-3}	log K_1	log K_2	ref
0.1	4.85 ± 0.01	4.91 ± 0.01	this work
0.3	4.51 ± 0.01	4.72 ± 0.01	this work
0.5	4.31 ± 0.02	4.62 ± 0.02	this work
0.7	4.27 ± 0.01	4.63 ± 0.02	this work
1.0	4.29 ± 0.01	4.66 ± 0.01	this work
0.1	4.76	4.99	28
0.1	4.60	5.17	29
0.1	4.80	−	30

A 50 mL acidic solution (0.1 mol·dm^{-3} $HClO_4$) of H_2tpps^{4-} ($2.59\cdot10^{-6}$ mol·dm^{-3}) was titrated with an alkali solution (0.1 mol·dm^{-3} NaOH). The $-\log[H^+]$ and absorbances from (200 to 800) nm were measured after addition of a few drops of titrant, and the procedure was continued up to the required pH of 12. The procedure was performed at different ionic strengths ranging from (0.1 to 1.0) mol·dm^{-3} $NaClO_4$.

The determination of the acidity constants of H_2tpps^{4-} is based on the relation $A = f(\text{pH})$.[26] The measured absorbance, A (with an interval of 2 nm), and $-\log[H^+]$ from the spectrophotometric titration were collected with the computer program Squad.[27] The program allows calculation of the different acidity constants that 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, with those reported in the literature.[28−30]

When an alkali solution was added to the acidic solution of H_2tpps^{4-}, the green color changes 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 ($H_4tpps^{2-} \rightleftharpoons H_3tpps^{3-} + H^+$) and the second deproto-

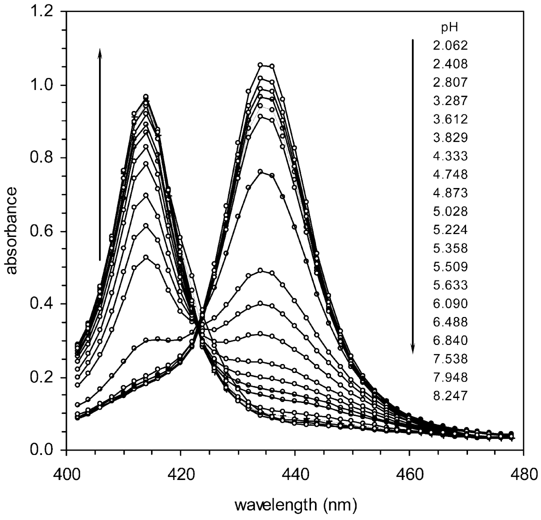

Figure 1. Visible absorption spectra of a series of aqueous solutions of H_2tpps^{4-} ($2.59\cdot10^{-6}$ mol·dm^{-3}) at 25 °C and different pH values.

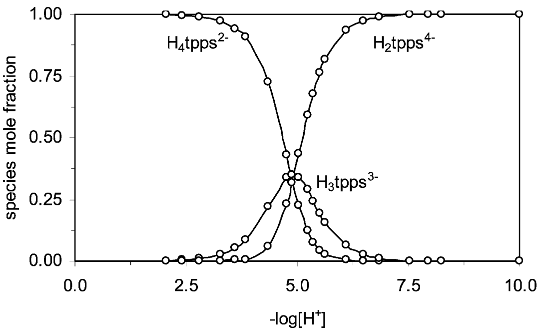

Figure 2. Distribution diagram of different protonated species of the ligand at 25 °C and 0.1 mol·dm^{-3} sodium perchlorate.

nation ($H_3tpps^{3-} \rightleftharpoons H_2tpps^{4-} + H^+$) 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 as only one reaction equilibrium.[30] In a similar study, Baker et al. have shown[31] that problems arise when only the Soret bands are considered. For example, H_2TPyP (tetrapyridylporphyrin) and H_2TMPyP [tetrakis(*N*-methyl-4-pyridyl)porphyrin] apparently have a single isosbestic point in the Soret, which indicates 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 isosbestic points and the monocation appears. To make this clear, we applied the computer program in two ways: (1) calculating only one protonation and (2) calculating a two-protonation equilibria. However, the sum of the squares error for the first assumption is about 10 times more than the second one. It is also interesting to note that log K in the first method is very close to log K_2 in the second method (log K = 4.89). Finally, with another isosbestic 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 Cadmium Ion. The cadmium cation shows a strong tendency to hydrolyze in aqueous solution, as demonstrated by several authors.[32] The formed hydrolytic species are very different and a variety of species are reported in the literature to date.[33] Hydrolysis of this metal ion becomes significant above pH = 7, usually in concentrated solutions, where polynuclear species are formed in small amounts before precipitation of cadmium hydroxide. Mononuclear hydrolysis products appear above pH = 8, but the low solubility of the hydroxide limits the concentration of cadmium. On the basis of literature data,[32,33] the formation of the following hydrolytic species have been reported: $Cd(OH)^+$, $Cd(OH)_2$, $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$, $Cd_2(OH)^{3+}$, and $Cd_4(OH)_4^{4+}$. To verify this, we performed several experiments with different concentrations of cadmium at the mentioned conditions, but our results showed a precipitation of cadmium hydroxide and thus a scattering in absorbance when the concentration of Cd^{2+} exceeded 0.01 mol·dm^{-3} at pH > 10, because of the low solubility of cadmium hydroxide in aqueous solution. Our results in this work are consistent with the formation of the first four mononuclear species, i.e. $Cd_p(OH)_q^{2p-q}$ (where $p = 1$ and $q = 1, 2, 3, 4$). The hydrolysis reactions and their formation constants are defined as

$$\begin{aligned}
&p\mathrm{Cd}^{2+} + q\mathrm{H_2O} \rightleftharpoons \mathrm{Cd}_p(\mathrm{OH})_q{}^{2p-q} + q\mathrm{H}^+ \\
&K_{pq} = ([\mathrm{Cd}_p(\mathrm{OH})_q{}^{2p-q}][\mathrm{H}^+]^q)/[\mathrm{Cd}^{2+}]^p \\
&\beta_{11} = K_{11}/K_\mathrm{w} \\
&\beta_{12} = K_{11}K_{12}/K_\mathrm{w}{}^2 \\
&\beta_{13} = K_{11}K_{12}K_{13}/K_\mathrm{w}{}^3 \\
&\beta_{14} = K_{11}K_{12}K_{13}K_{14}/K_\mathrm{w}{}^4
\end{aligned} \tag{3}$$

where K_w is the autoprotolysis constant of water at 25 °C and K_{11}, K_{12}, K_{13}, and K_{14} are the different hydrolysis constants of the cadmium ion species, respectively.[34]

The method of determination of β_{pq} is based on the relation $A = f(\mathrm{pH})$.[26] Absorbance (A) and $-\log[H^+]$ were measured for a solution containing Cd^{2+} [(1.0·10^{-4} to 2.2·10^{-4}) mol·dm^{-3}] with sufficient NaOH solution, as described. Treatment of the spectrophotometric data in the wavelength range (210 to 225) nm (with an interval of 5 nm) obtained during the titrations as a function of the H^+ concentration were conducted with the computer program Microsoft Excel Solver.[35] The program allows calculation of hydrolysis constants for different stoichiometry models. The degree of refinement then guides the choice between the models. Using the computer program, the data were fitted to the final equation for estimating the hydrolysis constants of eq 3. We used the Gauss−Newton nonlinear least-squares method in the computer program to refine the absorbance by minimizing the error squares sum from eq 4

$$U = \sum(A_{\mathrm{exp}} - A_{\mathrm{cal}})^2 \tag{4}$$

where A_{exp} is an experimental absorbance and A_{cal} is the calculated one. The computer program consisted of two different kinds of fitting, (a) graphical and (b) numerical. The final selection of the species was based on both graphical and numerical methods, considering in addition the various statistical criteria, i.e., sums of squared residuals and the differences of total concentration of Cd^{2+} used from those calculated.

Different models including polynuclear species with various hydroxyl groups were tested by the program. The models finally chosen, formed by $Cd(OH)^+$, $Cd(OH)_2$, $Cd(OH)_3^-$, and $Cd(OH)_4^{2-}$, resulted from satisfactory numerical and graphical fitting. The average value for various wavelengths calculated for the hydrolysis constant values of the species at different ionic strengths are listed in Table 2 together with the values reported in the literature.[32,33] The hydrolysis constant values determined in this work are in agreement with those reported before. The small differences are possibly due to the different experimental methods and a different background electrolyte to maintain the ionic strength. In Figure 3, the equilibrium distribution of various hydrolytic species of the cadmium cation are plotted versus $-\log[H^+]$. The first and second species, $Cd(OH)^+$ and $Cd(OH)_2$, are predominant at pH ≅ 10 and 11,

Table 2. Average Values of Hydrolysis Constants of Cd^{2+} Species $Cd_p(OH)_q^{2p-q}$, Where $p = 1$ and $q = 1, 2, 3, 4$, Respectively, at Different Ionic Strengths [(0.1 to 1.0) mol·dm^{-3} $NaClO_4$] and Literature Values

I / mol·dm^{-3}	log β_{11}	log β_{12}	log β_{13}	log β_{14}	ref
0.1	3.88 ± 0.03	7.49 ± 0.04	9.81 ± 0.09	10.87 ± 0.05	this work
0.3	3.65 ± 0.02	7.14 ± 0.05	9.55 ± 0.11	10.71 ± 0.06	this work
0.5	3.60 ± 0.01	7.02 ± 0.06	9.49 ± 0.10	10.62 ± 0.05	this work
0.7	3.63 ± 0.04	7.03 ± 0.04	9.51 ± 0.11	10.64 ± 0.07	this work
1.0	3.71 ± 0.04	7.11 ± 0.06	9.57 ± 0.04	10.72 ± 0.05	this work
0.1	4.0	7.7	10.3	12.0	32
0.1	3.7	7.21	8.04	7.77	33

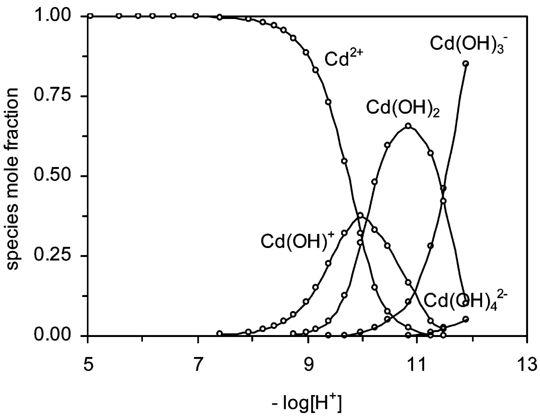

Figure 3. Distribution diagram of hydrolytic species of the cadmium ion versus hydrogen ion concentration at 25 °C and 0.1 mol·dm^{-3} $NaClO_4$.

respectively. The third species, $Cd(OH)_3^-$, becomes predominant at pH ≅ 12 and the last species, $Cd(OH)_4^{2-}$, starts to form in fairly low percentage at pH > 11.

Complexation of Cadmium Ion by H_2tpps^{4-}. Considering that the formation reaction rate of metalloporphyrins is very slow, evolution of absorption spectra should be carefully followed over a long time to be sure equilibrium is achieved. To overcome this problem, we have prepared 250 mL of an acidic stock solution (0.1 mol·dm^{-3}) of Cd^{2+} (1.65·10^{-7} mol·dm^{-3}) that is thermostated 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 (6.06·10^{-6} mol·dm^{-3}) was added to the respective flasks in the order (0.1, 0.2, 0.3,..., 5.0) mL and then 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 same procedure was performed for the other ionic strengths. Equilibrium was attained by allowing the solutions to stand over 24 h in the dark. During this time they were thermostated and agitated at 25 °C. The pH and UV−vis spectra of each solution were recorded versus wavelength of (200 to 800) nm, at 25 °C.

The complex $M_xH_yL_z^{(2x+y\text{-}4z)}$ 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}:

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

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

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. Treatment of the spectrophotometric data (every 2 nm) obtained during the titrations, as a function of the H^+ concentration, was 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 a $m \times n$ 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**

$$\mathbf{T} = \mathbf{CS} - \mathbf{R} \tag{7}$$

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.

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

Addition of the cadmium ion to the ligand solution caused significant changes in the spectra. Increasing the pH of solution from 2 to 12 caused a decrease in the ligand band at 435 nm and an increase in the Cd−tpps peak at 426 nm, which corresponds to the Cd−tpps complex species spectra obtained by direct synthesis previously.[7]

In a donor solvent like water, it is expected cadmium(II)−porphyrin possibly exhibits a preference for a six-coordinated structure[36] that is possibly similar to that of zinc(II)−porphyrins[16] and iron(III)−porphyrins.[37] The X-ray crystallographic and molecular studies of Zn(II)−porphyrin (5,10,15,20-tetraphenylporphyrin) have revealed the capability of the zinc ion to bind with two molecules of solvent in the axial position and occupy a position in the mean plane of the porphyrin as a ligand.[38] However, in this work, 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, ML_2, and hydroxo complex species (charges are omitted for simplicity). Interatomic distances between the metal ion and oxygen atom of the coordinated water molecules in the aquated metal ion $M(H_2O)^{2+}$ have been determined by the extended X-ray absorption fine structure (EXAFS) technique.[39] The Cd(II) ion is larger than the Zn(II) ion—the distance is 2.27 Å for Cd(II) and 2.07 Å for Zn(II)[39]—so the Cd(II) ion is not possibly expected to fit well inside the central hole of the porphyrin. This causes the Cd(II) ion to possibly locate near the cavity of the ligand or out-of-plane with respect to the unsubstituted pyrrolenic nitrogens. Such a feature is reflected in the following findings: the weaker stability constant of Cd−tpps than Zn−tpps, which better fits the cavity size of the ligand, and formation of very weak hydroxo complex species, which are consistent with the results obtained in this work. Also, a value for the MHL species was calculated by the program and the species was considered further, because the estimated error in its formation constant was acceptable and its inclusion improve the goodness of the fit. The models finally chosen, formed by the MHL and ML species, resulted in satisfactory numerical and graphical fitting, which are listed in Table 3 at different ionic strengths together with the values reported before.[6,7]

In Figure 4, the spectrophotometric titrations curves are presented for the Cd^{2+}−H_2tpps^{4-} system and also the different species of H_2tpps^{4-} alone at various wavelengths. Deprotonation of the ligand has been shown to induce a dramatic change in the molar absorption coefficients from curve a to curve b and for the complex species that is designated as c. Curve a is shown for H_4tpps^{2-} (Figure 4). At a higher concentration of sodium hydroxide, deprotonation has occurred and undergoes a large

Table 3. Average Values of Formation Constants of the Cadmium−Porphyrin System ($Cd-Htpps^{3-}$ and $Cd-tpps^{4-}$) at 25 °C and Different Ionic Strengths [(0.1 to 1.0) $mol \cdot dm^{-3}$ $NaClO_4$] Together with Values Reported in the Literature

I $mol \cdot dm^{-3}$	$-\log K_{Cd-Htpps^{3-}}$	$-\log K_{Cd-tpps^{4-}}$	ref
0.1	2.43 ± 0.02	9.94 ± 0.04	this work
0.3	2.94 ± 0.03	10.18 ± 0.06	this work
0.5	2.75 ± 0.05	10.31 ± 0.05	this work
0.7	2.73 ± 0.04	10.25 ± 0.04	this work
1.0	2.46 ± 0.04	9.86 ± 0.05	this work
0.1 ($NaNO_3$)	−	11.5	6
0.1 ($NaNO_3$)	−	10.27	7

shift to b. In the presence of the cadmium ion only one curve can be seen, c; this curve is designated for the complex species $(Cd-tpps)^{4-}$. In a kinetic study, a similar result has been found by Inamo et al.[6]

Figure 5 shows the equilibrium distribution of different species in terms of mole fractions of the Cd^{2+}-H_2tpps 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 complex species, Cd−Htpps, begins to form at pH ≅ 5.5 and the second, Cd−tpps, is the predominant species at pH > 10. The first and the only hydrolyzed species of cadmium ion, $Cd(OH)^+$, is formed in a very small amount at pH ≅ 9.5. The other hydrolyzed species of the cadmium ion were not computed due to their very low concentration in the presence of the ligand.

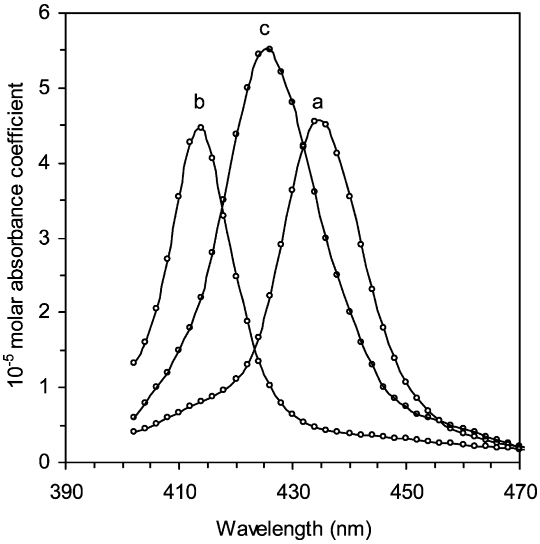

Figure 4. Molar absorption coefficients of a series of aqueous solutions of Cd^{2+} ($1.65 \cdot 10^{-7}$ $mol \cdot dm^{-3}$) and H_2tpps^{4-} ($6.06 \cdot 10^{-6}$ $mol \cdot dm^{-3}$) system at 25 °C and 0.1 $mol \cdot dm^{-3}$ sodium perchlorate: (a) H_4tpps^{2-}, (b) H_2tpps^{4-}, and (c) $Cd-tpps^{4-}$.

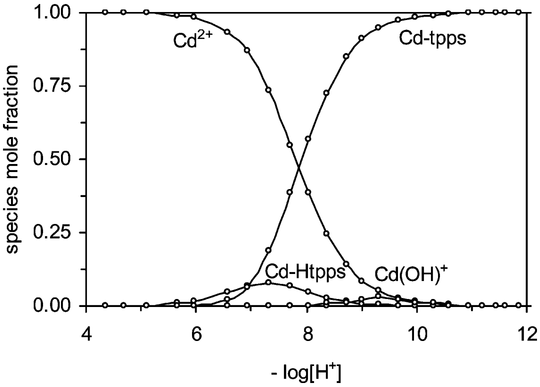

Figure 5. Distribution diagram of complex species of cadmium ion ($1.65 \cdot 10^{-7}$ $mol \cdot dm^{-3}$) and H_2tpps^{4-} ($6.06 \cdot 10^{-6}$ $mol \cdot dm^{-3}$) at different pH, 25 °C, and 0.1 $mol \cdot dm^{-3}$ sodium perchlorate.

Table 4. Parameters for the Dependence on Ionic Strength of Hydrolysis of Cadmium, Protonation of Porphyrin, and Complexation of $Cd-tpps^{4-}$ Constant Values at 25 °C

reaction	C	D
$Cd^{2+} + OH^- \rightleftharpoons Cd(OH)^+$	−0.86 ± 0.07	1.03 ± 0.05
$Cd^{2+} + 2OH^- \rightleftharpoons Cd(OH)_2$	−1.32 ± 0.05	1.43 ± 0.04
$Cd^{2+} + 3OH^- \rightleftharpoons Cd(OH)_3^-$	−0.35 ± 0.08	0.67 ± 0.06
$Cd^{2+} + 4OH^- \rightleftharpoons Cd(OH)_4^{2-}$	−0.47 ± 0.06	0.67 ± 0.04
$H_2tpps^{4-} + H^+ \rightleftharpoons H_3tpps^{3-}$	−0.58 ± 0.04	0.74 ± 0.03
$H_3tpps^{3-} + H^+ \rightleftharpoons H_4tpps^{2-}$	−0.16 ± 0.03	0.18 ± 0.05
$Cd^{2+} + H_2tpps^{4-} \rightleftharpoons Cd-Htpps^{3-} + H^+$	−1.76 ± 0.04	2.62 ± 0.05
$Cd-Htpps^{3-} \rightleftharpoons Cd-tpps^{4-} + H^+$	−6.59 ± 0.06	5.42 ± 0.04

Dependence on Ionic Strength. The dependence of the formation constants on ionic strength for the complex species can be described by the semiempirical equation[17−21,40−42]

$$\log K(I) = \log K(I^*) - f(I) + CI \tag{9}$$

where $f(I) = Z^*AI^{1/2}/(1 + BI^{1/2})$ and $K(I)$ and $K(I^*)$ are the formation constants of the actual and the reference ionic media, respectively. A is the parameter of the Debye−Hückel equation ($A = 0.51$ $mol^{-1/2} \cdot dm^{3/2}$ at 25 °C), $Z^* = \sum(\text{charges})_{\text{reactants}}^2 - \sum(\text{charges})_{\text{products}}^2$, C is an empirical parameter that is determined by fitting, and B is set equal to 1.5 $mol^{-1/2} \cdot dm^{3/2}$ (a small error in fixing B is absorbed in the linear term C[42]). Results of a series of investigations performed by Daniele et al., Sammartano et al.,[40−42] and Gharib et al.[17−21] showed that, when all the interactions occurring in the solution are considered, in the range ($0 \le I \le 1$) $mol \cdot dm^{-3}$, the empirical parameters are dependent on the stoichiometry of the formation reaction. If an approximate value of C is known, the stability constant can be determined for the variation of ionic strength from I^* to I by the equation

$$\log K(I) = \log K(I^*) - f(I, I^*) + C(I - I^*) \tag{10}$$

where

$$f(I, I^*) = Z^*A[I^{1/2}/(1 + 1.5I^{1/2}) - I^{*1/2}/(1 + 1.5I^{*1/2})] \tag{11}$$

and I and I^* are the ionic strength of the solution by the appropriate electrolyte. A preliminary analysis of the data showed that if a fixed value is assigned to C, the fit with eq 11 is not always good over the whole range of ionic strength from (0.1 to 1.0) $mol \cdot dm^{-3}$. This equation may be useful for small changes of ionic strength, but a better fit is obtained by adding a further term of the form $DI^{3/2}$ (D is another adjustable parameter). Therefore, the data were fitted to eq 12.

$$\log K(I) = \log K(I^*) - f(I, I^*) + C(I - I^*) + D(I^{3/2} - I^{*3/2}) \tag{12}$$

It is noticeable that the introduction of the term $D(I^{3/2} - I^{*3/2})$ very often improves the goodness of the fit. For example, for the $\log K_{101}$ in sodium perchlorate media, from eq 12, we obtained two sets of values depending on whether or not we take into account the term in D:

$$C = -1.21, U = 5.10 \cdot 10^{-1}$$

$$C = -6.59, D = 5.42, U = 7.21 \cdot 10^{-5}$$

The squares sum, U, shows that there is a significant improvement in the fit when the D term is introduced.

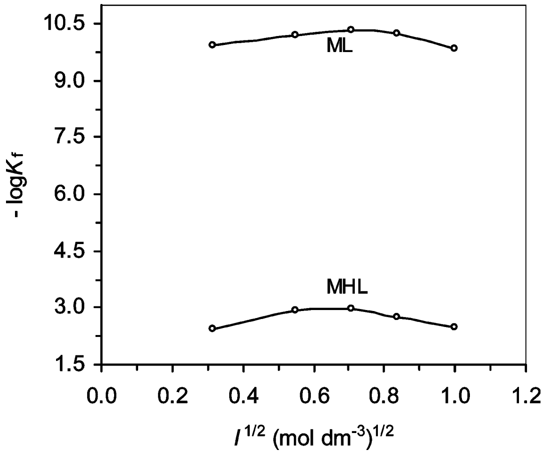

Figure 6. Plots of pK_f versus the square root of the ionic strength at 25 °C.

The parameters for the dependence on ionic strength (C and D) were calculated by the fitting method and are reported in Table 4. The dependence of log K on ionic strength determined in $NaClO_4$ as background electrolyte (Figure 6) shows a regular trend and are in good agreement with other complex species.[17−21,40−42] Our previous results on the ionic strength dependence of complex formation constants[17−21] and this work reveal that the log K values are nearly always at their minimum at an ionic strength range (0.3 to 0.7) $\text{mol}\cdot\text{dm}^{-3}$, which is a characteristic of the curve log $K = f(I)$. According to the theory of electrolytic solutions,[43] the $AI^{1/2}$ term in eq 12 accounts for Coulombic interactions between ions screened by the ion atmosphere, while the BI term accounts for disturbances in the ion−solvent interaction. At low ionic strength, less than 0.1 $\text{mol}\cdot\text{dm}^{-3}$, these interactions are of primary importance. However, as the ionic strength increases, the ionic atmosphere becomes more compressed and screens the ionic charges more effectively, so that intermolecular interactions (dipole−dipole or multipole−multipole) become more important. These forces at higher ionic strength possibly have the primary role between the ions and contribute to the C and D terms in eq 12.

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