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Study of the Aqueous Equilibrium System Involving *meso*-Tetrapyridylporphine, Alkali Metal Ions, and Hydrogen Ions

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Hydrogen ion and alkali metal ion complexes of *meso*-tetrapyridylporphine (PH_2) were examined spectrophotometrically in aqueous media. Our data can be interpreted quantitatively and self-consistently if we assume the existence of an equilibrium scheme involving the free base PH_2, the monocation PH_3, the dication PH_4, and two metal–porphyrin complexes PH_2M and PH_3M. Equilibrium constants for the system were obtained in the range 15–55 °C. The metal complexes PH_2M and PH_3M appear to be spectrophotometrically identical with PH_3 and PH_4, respectively, and it seems probable that there is a definite relationship between the core charge of the porphyrin molecule and the spectral character of the porphyrin moiety.

Introduction

For many years there has been considerable interest in the possible existence of the sitting-atop complex (SAT) precursor to metalloporphyrin formation suggested originally by Fleischer and Wang[1] to explain their observations on metal ion incorporation by protoporphyrin dimethyl ester in acetone. Fleischer, Choi, Hambright, and Stone[2] found that many metal ions apparently form 1:1 SAT complexes in aqueous *meso*-tetrapyridiniumporphine (TpyP) solutions. Recently Baker, Hambright, and Wagner[3] reported acid–base and kinetic studies of *meso*-tetra-4-methylpyridylporphine (TMpyP) in which they found that the values of pK_1' and pK_2' defined in the equations

$$PH_3 = PH_2 + H^+, \quad K_1'$$
$$PH_4 = PH_3 + H^+, K_2'$$

appeared to increase with increasing ionic strength. [Note: we are using the symbols PH_3 and PH_4 to represent the monocation and the dication, respectively. The charges are omitted.] Thus as $NaNO_3$ or NaCl was added, the concentration of the diprotonated porphyrin cation, PH_4, appeared to increase. On the basis of their results Baker et al. concluded that there is no evidence for the existence of SAT complexes in aqueous solutions containing TpyP or TMpyP.

The SAT complex does get strong support from the study by Mackay and Letts[4] of the interaction of Cu(II) ion, *meso*-tetraphenylporphine (TPP), and triphenylphosphine in a benzene-in-water microemulsion in which they observed the stabilization of a copper–porphyrin complex in the interphase region of the system.

We have decided to reexamine the possibility that *meso*-tetrapyridylporphine (TpyP) may form stable, long-lived metallo complexes. In the first phase of this work, which is reported here, we have studied the spectra of TpyP in aqueous solutions as a function of temperature (15–55 °C), pH (1–2), and concentration of $LiNO_3$, $NaNO_3$, and KNO_3 (0.1–3 M); the concentration of TpyP was always roughly 8×10^{-5} M. In the pH range of our studies all pyridyl residues of TpyP are protonated. Alkali metal ions do not incorporate to form true metalloporphyrins under the conditions of our experiments.

Table I. Extinction Coefficients ($\times 10^{-3}$) for the Porphyrinic Species in Solution[a]

Species	Band I (6380 Å)	Band II (5850 Å)	Band III (5530 Å)	Band IV (5170 Å)
PH_2	2.1	5.7	5.5	18.8
PH_3	~0.0	5.6	8.0	~0.0
PH_4	16.0	13.9	3.3	1.4

[a] The extinction coefficients, ϵ_i, are listed for the three porphyrinic species at the four wavelengths at which free-base TpyP (or PH_2) exhibits maxima.

Experimental Section

The visible absorbance of aqueous solutions of TpyP was monitored with the Cary 14 spectrophotometer as a function of temperature, pH, and concentration of added electrolytes, $LiNO_3$, $NaNO_3$, and KNO_3. All solutions were prepared volumetrically from doubly distilled water. The temperature was controlled to ±0.05 °C. The pH was varied by using various concentrations of HNO_3. The nitric acid and metal nitrates were reagent grade and were used without further purification. The TpyP was prepared by the method of Longo, Finarelli, and Kim.[5]

Results

For convenience we shall refer to solutions containing HNO_3 as acidified or acidic solutions and to solutions containing both HNO_3 and a metal salt as metal solutions.

Visible spectra of the free-base porphyrin (PH_2) and diprotonated cation porphyrin (PH_4) are respectively four and two banded. The bands of PH_2 are numbered from the long-wavelength end of the spectra. See Table I. The complete spectrum of the monocation (PH_3) was not determined quantitatively but it is definitely three banded.

Band IV absorbance always increases with increasing temperature of pH and decreases with increasing metal salt concentration; band I behaves in an opposite manner. At a pH >1.45 a sharp cross point develops in the isotherms at

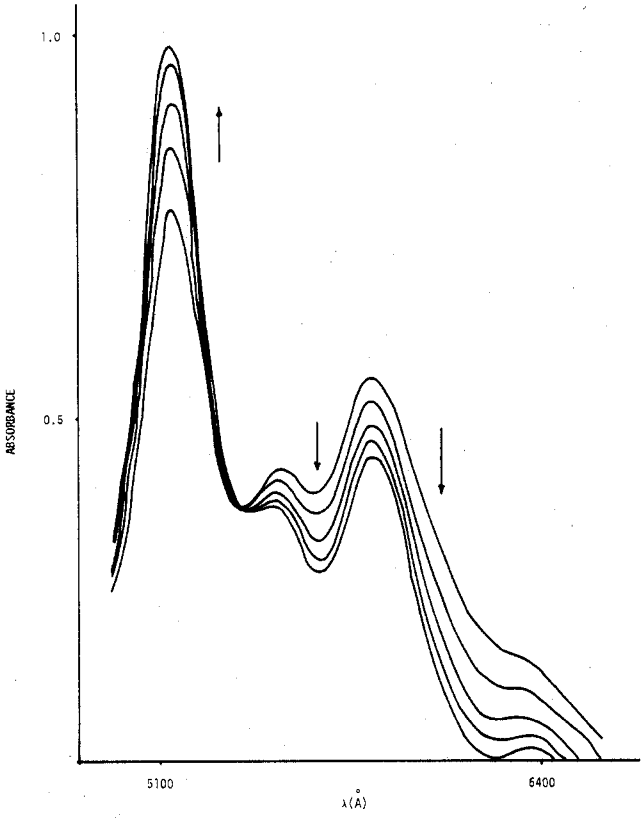

Figure 1. Spectral isotherms for $[LiNO_3] = 0.1$ M and $[H^+] = 1.12 \times 10^{-2}$ M from 15 to 55 °C. The arrows point in the direction of increasing temperature.

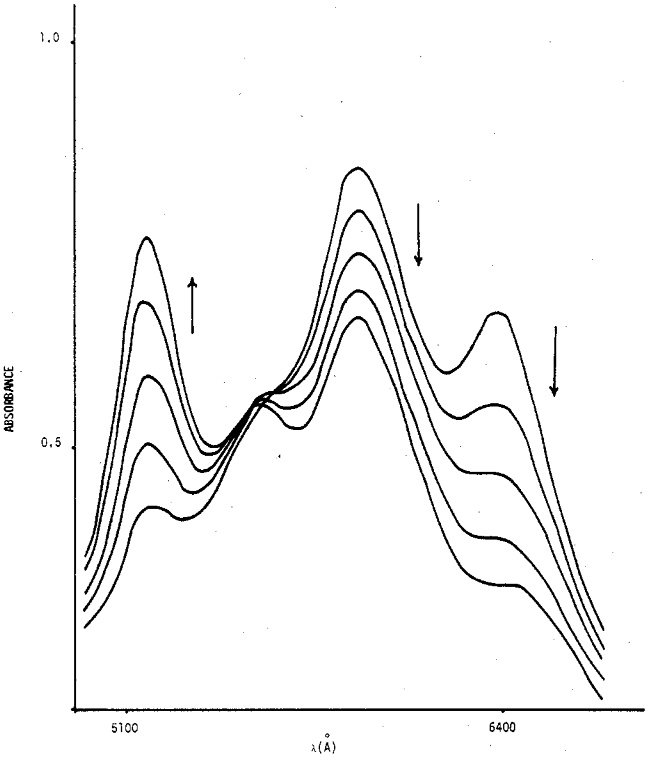

Figure 2. Spectral isotherms for $[LiNO_3] = 1.0$ M and $[H^+] = 1.12 \times 10^{-2}$ M from 15 to 55 °C.

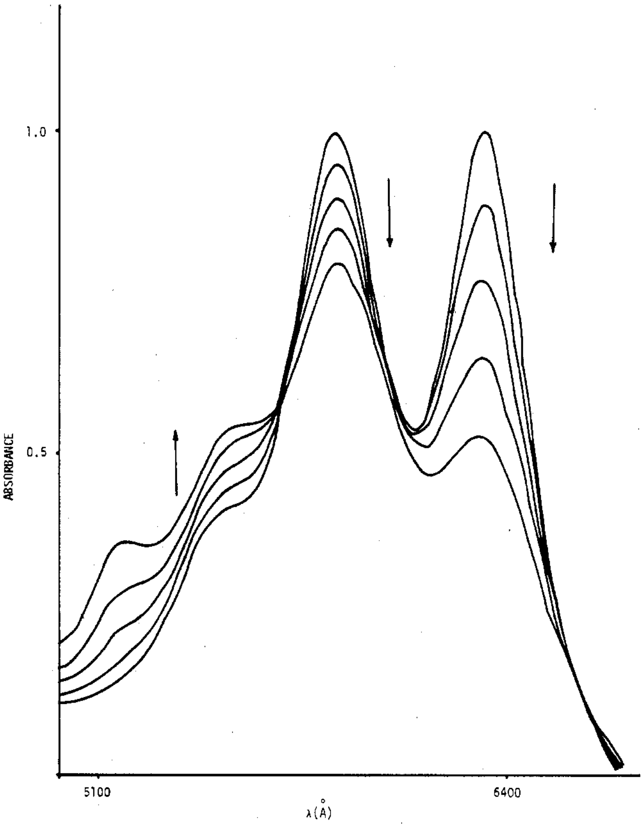

Figure 3. Spectral isotherms for $[LiNO_3] = 3.0$ M and $[H^+] = 1.12 \times 10^{-2}$ M from 15 to 55 °C.

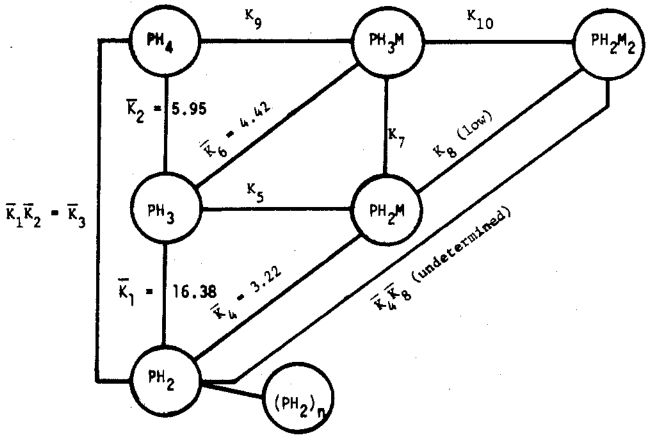

Figure 4. The equilibrium network using constants for the $LiNO_3$ system at 25 °C.

approximately 5420 Å in acid solutions. In metal salt solutions the apparent concentration of PH_4 is much larger than in equally acidic solutions containing no metal salts. Figures 1–3 show how differences in pH and $LiNO_3$ concentration affect the development of the isotherms. Under the same conditions solutions of $LiNO_3$, $NaNO_3$, and KNO_3 give very similar spectra.

An examination of the spectra from both acidic and metal salt solutions shows that, generally, the cross points in the curves are not sharp, but above pH 1.45 in acid solutions the cross points are quite sharp; as the pH decreases below 1.45 the cross points tend to traverse the head of band III, finally producing intersections between bands II and III. In metal salt solutions as the metal salt concentration increases, there is a generation of three cross points, two between bands I and II, which are random, and a third on the red side of band I (6700 Å), which is fairly constant. Solutions containing higher concentrations of both acid and metal salt show a more pronounced cross point scatter at 6700 Å. When potassium acetate and KCl were used in place of KNO_3, the solutions showed the same general characteristics. Calculations show that the effect of temperature on solution volume and, therefore, on concentration is negligible. Thus, the cross point scatter must be due to the presence of more than two porphyrinic species.

The absorbance data for these solutions are voluminous and will not be reproduced here. The interested reader is therefore referred to ref 6.

Calculation of Equilibrium Constants

An equilibrium scheme which may govern the state of our system under the most general conditions is presented in Figure 4. Some of the reactions implied by the scheme are given here along with the associated equilibrium constants

$PH_2 + H^+ = PH_3,\ K_1$
$PH_3 + H^+ = PH_4,\ K_2$
$PH_2 + 2H^+ = PH_4,\ K_1K_2$
$PH_2 + M^+ = PH_2M,\ K_4$
$PH_3 + M^+ = PH_2M + H^+,\ K_5$
$PH_3 + M^+ = PH_3M,\ K_6$
$PH_2M + H^+ = PH_3M,\ K_7$
$PH_2M + M^+ = PH_2M_2,\ K_8$
$PH_4 + M^+ = PH_3M + H^+,\ K_9$
$PH_3M + M^+ = PH_2M_2 + H^+,\ K_{10}$

Using the conclusion of Mackay and Letts[4] that the spectrum (shape and extinction coefficients) of a particular porphyrin species depends primarily on the charge of the porphine nucleus, it is possible to calculate the concentrations of all porphyrinic species in solution. Specifically, we have assumed that $\epsilon_{PH_3} = \epsilon_{PH_2M}$ and that $\epsilon_{PH_4} = \epsilon_{PH_3M} = \epsilon_{PH_2M_2}$.

The extinction coefficients for PH_2, PH_3, and PH_4 at four wavelengths are listed in Table I. We obtained the ϵ values for PH_2 in aqueous solutions containing 40% methanol and for PH_4 in aqueous 3 M HNO_3 solutions. We assumed that the monoprotonated species, PH_3, had no absorption at 6380 and 5170 Å. Our assumptions are justified a posteriori.

In order to determine the equilibrium constants specified by the scheme shown in Figure 4 the equilibrium concentrations of all species must be known. The equilibrium concentrations can be calculated from the solution of the four equations (e.g., eq 1) for absorbance at the four wavelengths for which we know the extinction coefficients of the porphyrinic species and the mass balance equation.

$$A^i = \epsilon^i_{PH_2} C_{PH_2} + \epsilon^i_{PH_3}(C_{PH_3} + C_{PH_2M}) + \epsilon^i_{PH_4}(C_{PH_4} + C_{PH_3M} + C_{PH_2M_2}) \qquad (1)$$

$$C_1 = C_{PH_2} + C_{PH_3} + C_{PH_2M} + C_{PH_4} + C_{PH_3M} + C_{PH_2M_2} \qquad (2)$$

A^i is the absorbance at the ith band of the free base porphyrin; the value of i ranges from I to IV. C_T is the total concentration of porphyrinic species.

Following Mackay and Letts we have assumed that $\epsilon_{PH_3} = \epsilon_{PH_2M}$ and $\epsilon_{PH_4} = \epsilon_{PH_3M} = \epsilon_{PH_2M_2}$, so it is generally impossible to obtain the concentrations of all porphyrinic species in our proposed equilibrium scheme. In acidified solutions the complexity of the system is reduced because only three porphyrinic species are present. By using equations of the form of eq 1 and the mass balance equation it is possible to obtain the equilibrium concentrations of PH_2, PH_3, and PH_4 in acid solutions, and, hence, we were able to calculate K_1 and K_2. In these calculations we assumed that $\epsilon^I_{PH_3} = \epsilon^{IV}_{PH_3} = 0$. The values of these equilibrium constants are presented in Table II.

The facts that K_1 and K_2 are fairly constant and self-consistent and that plots of ln K vs. $1/T$ for both K_1 and K_2 are linear (with slopes corresponding to enthalpy changes of -3.2 kcal for ΔH_1 and -6.0 kcal for ΔH_2) justify our assumption that $\epsilon^I_{PH_3} = \epsilon^{IV}_{PH_3} = 0$.

Table II.[a] Equilibrium Constants, K_c, for Protonation Processes Calculated from Concentration (Aqueous Acid Solutions)

	15 °C	25 °C	35 °C	45 °C	55 °C
$\overline{K}_1$	24.7	20.7	17.3	14.6	12.6
SDM	2.1	1.3	0.9	0.8	0.9
LSV	24.8	20.5	17.2	14.5	12.4
$\overline{K}_2$	10.1	7.5	5.5	4.0	3.0
SDM	0.8	0.6	0.5	0.4	0.4
LSV	10.7	7.5	5.4	4.0	2.9
$\overline{K}_3 = \overline{K}_1\overline{K}_2$	249	156	94.4	58.6	36.0
SDM	24	15.0.	8.3	4.1	3.2
LSV	253	150	90.0	58.2	37.8

$$\Delta H_1 = 3240,\ \Delta H_2 = 6060,\ \Delta H_3 = 8930 \text{ cal/mol}$$

$$\Delta S_1 = -4.87,\ \Delta S_2 = -16.3,\ \Delta S_3 = -20.0 \text{ cal/(mol K)}$$

[a] $\overline{K}_n$ is the average value of K_n; SDM is the standard deviation; LSV is the value of K_n determined from least-squares analysis of ln K vs. $1/T$.

Table III.[a] Equilibrium Constants, K_a, for Protonation Processes–Activity Corrected

	15 °C	25 °C	35 °C	45 °C	55 °C
$\overline{K}_1$	19.62	16.38	13.59	11.42	9.88
SDM	2.02	1.19	0.91	0.78	0.83
LSV	19.57	16.19	13.55	11.48	9.82
$\overline{K}_2$	8.02	5.95	4.30	3.15	2.33
SDM	0.56	0.43	0.35	0.25	0.25
LSV	8.57	5.99	4.28	3.13	2.33
$\overline{K}_3$	156.71	97.36	58.44	35.99	22.94
SDM	17.28	9.00	4.56	2.02	1.26
LSV	163.73	96.05	58.33	36.55	23.56

$$\Delta H_1 = -3240.0,\ \Delta H_2 = -6116.7,\ \Delta H_3 = -9105.6 \text{ cal/mol}$$

$$\Delta S_1 = -5.3336,\ \Delta S_2 = -16.957,\ \Delta S_3 = -21.469 \text{ cal/(mol K)}$$

[a] In Tables III–VI all porphyrinic species are assumed to have a diameter of 17.5 Å in solution. The species PH_2 is assumed to possess a charge of 0.9+; PH_3, 1.9+; PH_4, 2.9+; PH_2M, 1.9+; PH_2M_2, 2.9+; and PH_3M, 2.9+.

We also calculated the equilibrium constants K_1 and K_2 in terms of activities by application of the extended Debye–Hückel theory which requires the values of the charge and diameter of ionic species. In our calculations we varied the diameter of the porphyrin from 4.08 to 25 Å. (The diameters of the species PH_2, PH_3, and PH_4 are assumed to be equal.) The lowest value, 4.08 Å, is the distance between opposite pyrrolyl nitrogens, 8.81 Å is the distance between opposite pyrrolyl β–β bonds, and 17.5 Å is the distance between opposite pyridyl nitrogen atoms. We varied the charges from 0, 1+, and 2+ to 4+, 5+, and 6+ for the species PH_2, PH_3, and PH_4, respectively. Selection of the lowest charges on the ions was made by considering the possibility that the fully protonated pyridyl groups might have charge interaction with the reactive central site of the molecule. The most self-consistent set of equilibrium constants was obtained with d = 17.5 Å and charges of 0.93+, 1.93+, and 2.93+. The results of this calculation are presented in Tables II and III under the headings $\overline{K}_1$ and $\overline{K}_2$.

We calculated the values of K_1 and K_2 from data obtained in salt solutions assuming that the metal ions were not directly involved in any porphyrin equilibrium. In general, the largest deviations in K_1 were noted at the lowest H^+ concentration and highest salt concentration. At 25 °C K_1 in acid solutions is 20.7; in 3 M $LiNO_3$ at pH 1.9 values exceeding 298 are found. The same variation is found with K_2: at 25 °C K_2 in acid solutions is 7.5; in the $LiNO_3$ solution values of 161 are found. In addition, the values of K_1 and K_2 obtained from salt

Table IV. Equilibrium Constants for $LiNO_3$ Solutions

	15 °C	25 °C	35 °C	45 °C	55 °C
$\bar{K}_{PH_2M_2}$	24.7	16.4	11.0	7.0	4.4
SDM	50.7	32.6	21.7	13.6	7.9
LSV	6.5	4.2	2.8	1.9	1.3
$\bar{K}_{PH_3M}$	102.0	71.7	50.4	33.7	22.8
SDM	24.8	14.1	10.3	7.9	6.3
LSV	101.0	68.6	47.7	33.9	24.6
$\bar{K}_4$	3.53	3.22	2.88	2.49	2.19
SDM	3.35	2.76	2.16	1.72	1.42
LSV	2.62	2.34	2.10	1.90	1.73
$\bar{K}_6$	4.97	4.42	3.71	2.93	2.32
SDM	2.81	0.87	0.75	0.68	0.64
LSV	5.17	4.23	3.51	2.95	2.50

$\Delta H(PH_2M_2) = -7598$, $\Delta H(PH_3M) = -6648$, $\Delta H_4 = -1946$, $\Delta H_6 = -3408$ cal/mol

$\Delta S(PH_2M_2) = -22.6$, $\Delta S(PH_3M) = -13.9$, $\Delta S_4 = -4.83$, $\Delta S_6 = -8.56$ cal/(mol K)

Table V. Equilibrium Constants for $NaNO_3$ Solutions

	15 °C	25 °C	35 °C	45 °C	55 °C
$K_{PH_2M_2} = K_4K_8$	29.0	18.4	12.3	9.36	5.89
SDM	47.2	34.1	22.2	14.1	10.6
LSV	7.69	4.97	3.30	2.25	1.57
$\bar{K}_{PH_3M} = K_1K_6$	101.0	71.0	49.5	34.0	23.6
SDM	21.3	13.3	7.69	7.60	5.12
LSV	102.0	68.4	46.9	33.0	23.7
$\bar{K}_4$	2.78	2.69	2.45	2.09	1.99
SDM	2.02	1.92	1.18	1.19	1.21
LSV	2.37	2.13	1.93	1.76	1.62
$\bar{K}_6$	5.13	4.34	3.65	2.90	2.40
SDM	1.08	0.87	0.56	0.58	0.52
LSV	5.22	4.22	3.46	2.87	2.41

$\Delta H(PH_2M_2) = -7460.0$, $\Delta H(PH_3M) = -6870$, $\Delta H_4 = -1790$, $\Delta H_6 = -3630$ cal/mol

$\Delta S(PH_2M_2) = -21.8$, $\Delta S(PH_3M) = -14.6$, $\Delta S_4 = -4.50$, $\Delta S_6 = -9.31$ cal/(mol K)

Table VI. Equilibrium Constants for KNO_3 Solutions

	15 °C	25 °C	35 °C	45 °C	55 °C
$\bar{K}_{PH_2M_2}$	4.82	3.65	2.07	1.72	1.28
SDM	4.23	3.14	2.21	1.45	0.87
LSV	3.29	2.13	1.41	0.96	0.67
$\bar{K}_{PH_3M}$	77.70	57.97	38.38	27.71	18.50
SDM	12.02	11.87	8.31	5.37	4.04
LSV	76.84	52.99	37.42	27.03	19.91
$\bar{K}_4$	2.71	2.50	2.22	1.95	1.65
SDM	1.52	1.47	1.18	0.96	0.78
LSV	2.54	2.18	1.89	1.65	1.46
$\bar{K}_6$	3.96	3.57	2.81	2.41	1.88
SDM	0.61	0.73	0.60	0.46	0.41
LSV	3.92	3.27	2.76	2.35	2.02

$\Delta H(PH_2M_2) = -7440$, $\Delta H(PH_3M) = -6340$, $\Delta H_4 = -2590$, $\Delta H_6 = -3100$ cal/mol

$\Delta S(PH_2M_2) = -23.4$, $\Delta S(PH_3M) = -13.4$, $\Delta S_4 = -7.14$, $\Delta S_6 = -8.05$ cal/(mol K)

solution data, using activity-corrected data and assuming no direct participation of metal ions in any equilibrium process involving the porphyrin, show significant deviation among themselves and from the initial acid solutions; K_1 and K_2 become less different from the initial acid solution values at higher hydrogen ion concentration and lower salt concentration.

Since the presence of salts greatly affects the apparent values of K_1 and K_2, it would not be totally unreasonable to infer, as did Fleischer and Webb,[7] that metal ions may be directly involved in metal–porphyrin complex formation. This idea justifies the upper portion of the equilibrium scheme of Figure 4, in which the metal–porphyrin complexes PH_2M, PH_3M, and PH_2M_2 are involved.

Initially the calculation of the K_i's from metal solution data utilizes the values of K_1 and K_2 found in acid solutions. We first calculate the concentrations of PH_3 and PH_4 predicted from the concentrations of PH_2 and H^+ in solution. If the observed absorbances indicate concentrations of PH_3 and PH_4 greater than the concentrations of PH_3 and PH_4 calculated from K_1 and K_2, the difference is assigned to a metal-containing derivative of equivalent charge. This is not straightforward in the case of the dication (PH_4) as two spectrally equivalent metallo derivatives, PH_3M and PH_2M_2, exist. Therefore, the apparent excess of dication was assigned to either the PH_3M or the PH_2M_2 species, i.e.

$$[PH_3M] \text{ (or } [PH_2M_2]) = [PH_4](\text{from absorbance data}) - [PH_4](\text{from } K_1 \text{ and } K_2)$$

Then we calculated the equilibrium constants K_{PH_3M} and $K_{PH_2M_2}$

$$PH_2 + H^+ + M^+ = PH_3M; \quad K_{PH_3M} = K_1K_6$$

$$PH_2 + 2M^+ = PH_2M_2; \quad K_{PH_2M_2} = K_4K_8$$

If one of the defined equilibria is predominant and the other almost inoperative, a self-consistent data set will be developed with only one equilibrium constant, K_{PH_3M} or $K_{PH_2M_2}$. If both processes are significant, there will be a lack of self-consistency when a large number of data are treated with the mass balance equations. Our analysis shows that the concentration of PH_2M_2 is either very low or zero and only the equilibrium governed by K_{PH_3M} is significant. The standard deviations of the means calculated from various $K_{PH_2M_2}$'s were equal to or greater than the $K_{PH_2M_2}$'s; see Tables IV–VI. We were able to obtain self-consistency without the use of $K_{PH_2M_2}$.

In all, more than 80 solutions of different concentrations were examined; the spectral data from these solutions was used to determine the K_n's. In no instance did we obtain K_n values with data from less than five solutions of different concentration.

Discussion of the Total Equilibrium System

The total equilibrium system found with acid- and salt-containing solutions has been diagrammed in Figure 4 using the data from $LiNO_3$ solutions at 25 °C as an example.

At equivalent activities for different solutions, $K_i^{Li} > K_i^{Na} > K_i^{K}$, where K_i^{M} is any equilibrium involving a metalloporphyrin complex. This is found, practically without exception, in all solutions studied. The process governed by K_i^{M} is normally in the direction of product formation, and, of course ΔG is negative for that direction. At higher metal salt concentration, saturation occurs via paths governed by the constants K_4, K_6, and K_7, and large concentrations of PH_3M occur.

Relatively high concentrations of the PH_2 species exist in solution at higher pH in the absence of metal ion. At a pH slightly greater than 2 polymeric porphyrins may be present. This conclusion is reached on the basis of a material balance test of our analysis of acid solutions. Polymerization is not detectable at higher acid and/or metal ion concentrations. The process of polymerization, like other equilibrium processes, is easily reversed and appears to depend upon $[H^+]$

$$2PH_2 = (PH_2)_2 + 2H^+; \quad 2 \times 10^{-2} \simeq K_D(25\ °C)$$

(The product H^+ ion is assumed to be released from protonated pyridyl groups.) This insinuates either that aggregation is favored immediately after deprotonation or that aggregation tends to favor a deprotonation of the porphyrin. This would tend to agree with the work of Pasternack et al., who found that the electrolyte concentration would be required to be very low if aggregation is to be noted for TpyP.[8]

Although we assumed that PH_2M and PH_3M are spectrally equivalent to PH_3 and PH_4, respectively, it is probable that they have slightly different extinction coefficients at the monitored bands. This can account for some of the variation in the calculated values of K_i^M. These changes in extinction coefficient must necessarily be small as errors such as negative concentrations that would otherwise disrupt the computer analysis never occurred.

Calculations were made for the species PHM, proposed by Hambright et al. in the reaction[8]

$$PH_2 + M^+ = PHM + H^+$$

The introduction of this reaction into our proposed equilibrium network proved to be deleterious to the self-consistency of the system. Equilibrium constants varied by factors of 10–100 when this process was introduced.

At high metal salt concentrations uncorrected activity effects and swamping of the equilibrium paths governed by K_4, K_6, and K_7 tend to produce the results initially observed by Hambright: an apparently pure dication spectrum. This is a condition that we observed for many of our solutions, but the effect is too large to be considered as an activity effect on the protonation equilibria as Hambright suggested.[3] The metalloporphyrin complex PH_3M of the alkali metal salts is probably responsible for the apparent wide variation of the values for the protonation constants noted by Pasternack et al.[9,10] and Hambright et al.[3] This effect can probably occur with all water-soluble porphyrins of cationic or anionic nature.

It is important to note that, while aggregation of the anionic porphyrins is enhanced in the presence of supposedly inert electrolytes, we have found as did Pasternack that the cationic porphyrins exhibit just the reverse effect.[9,10] This would be expected since the enhancement of aggregation of anionic prophyrins and reduction with the cationic porphyrin TpyP probably depend upon a Coulombic repulsion term. Formation of a metalloporphyrin complex in the case of TpyP will tend to increase intermolecular repulsion, whereas formation of metalloporphyrin complexes with anionic porphyrins tends to reduce the repulsion. The ability to enhance or reduce this repulsion via the formation of a porphyrin–metal complex is probably paramount in the consideration of the tendency to aggregate. This effect also explains the different literature values of the pH above which TpyP is insoluble (between pH 2 and 4 depending upon the ionic strength of the solution). The molecule is basically hydrophobic with the charged portions of the macrocycle conferring hydrophilic character to a varying degree; the overall charge of the molecule determines whether the porphyrin is water soluble or not.

An examination of the enthalpy changes associated with the steps in our equilibrium network shows some interesting effects. The enthalpy decrease for the addition of a proton or a metal ion to either PH_3 or PH_2M is greater than the enthalpy decrease for the same additions to the free-base porphyrin. This supports the suggestion of Hambright,[11] who on the basis of kinetic data inferred that the addition of a proton to the porphyrin nuclei would result in ring buckling making the inner nitrogen atoms more accessible to attack. Also when M^+ exchanges with H^+ as in the paths governed by K_5 and K_9, the enthalpy change is positive. For all other processes in our scheme the enthalpy decreases. This suggests that the proton is more firmly bound to the porphyrin than the alkali metal ions, a result which is not surprising. The entropy changes for all processes are negative except for the two governed by K_5 and K_9. In these cases $\Delta S > 0$. Again this result is not surprising since most of the processes involve either proton or metal ion capture. These are expected to be accompanied by an entropy decrease.

In summary our spectrophotometric study of TpyP solutions has suggested an equilibrium scheme for which we have been able to derive a set of the equilibrium constants which are fairly nonvariable and self-consistent. We believe that this study indicates that there are porphyrin–metal complexes (perhaps SAT complexes) which are not true metalloporphyrins. It is finally important to emphasize that our analysis was made possible by adopting the hypothesis of Mackay and Letts that the extinction coefficients are primarily dependent on the charge of the porphyrin moiety.

Registry No. PH_2, 16834-13-2; PH_3, 62107-59-9; PH_4, 62107-60-2; PH_2Li_2, 62107-61-3; PH_3Li, 62107-62-4; PH_2Li, 62107-63-5; PH_2Na_2, 62107-64-6; PH_3Na, 62107-65-7; PH_2Na, 62107-69-1; PH_2K_2, 62107-66-8; PH_3K, 62107-67-9; PH_2K, 62107-70-4.

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