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Equilibrium Studies on Mercury(II)–Porphyrins in Aqueous Solution

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Introduction

Recently we have reported [1] on mercury(II)–H_2TPPS [2] equilibrium in aqueous solutions. The system was treated as a single equilibrium since the absorption spectra of the solution had an apparent isosbestic point during the titration. By comparison of the final spectrum with that of known mercury(II)–tetraphenylporphyrin [3] the composition of the resultant species were assumed to be two mercury(II) ions to one porphyrin. Since then we have studied this system under varying conditions employing in addition to H_2TPPS, a peripherally positively charged porphyrin, H_2TAPP, in water. Results of these studies have altered our conclusions drastically and are presented here.

Experimental

Experimental details are the same as reported earlier [1]. Additional details are the following: H_2TAPP was synthesized as in the literature [4]. An approximately 5×10^{-5} *M* solution of H_2TAPP was used in the titrations with mercury(II) ions. Titrations with both porphyrins were also recorded in the Soret region (390–450 nm) using a 0.1 cm pathlength cuvette. Titrations employing further dilution of both H_2TPPS (2.51×10^{-7} *M*) and H_2TAPP (2.45×10^{-7} *M*) were performed and recorded in the Soret region using a 10.0 cm pathlength cuvette.

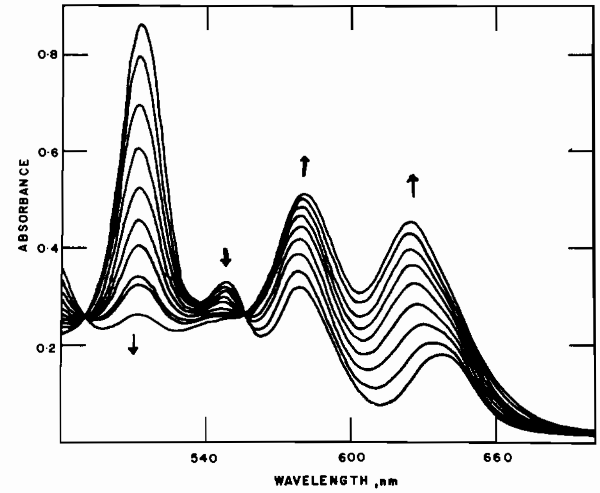

Fig. 1. Changes in the spectrum of H_2TAPP solution ($\sim 10^{-5}$ *M*) during the titration with Hg^{2+} (path length of cuvette = 1.0 cm).

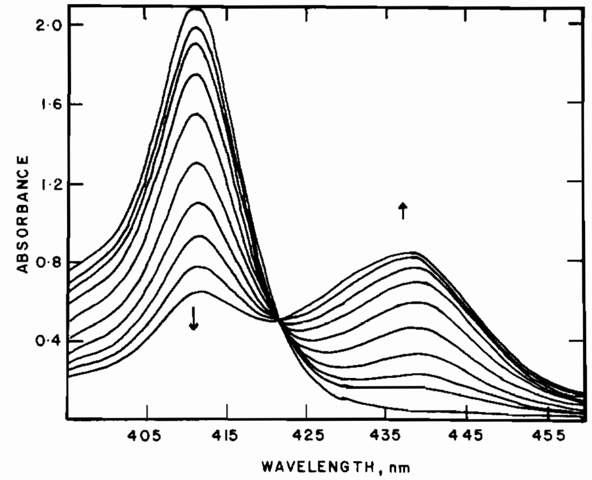

Fig. 2. Changes in the spectrum of H_2TAPP (5.12×10^{-5} *M*) during the titration with Hg^{2+} (path length of the cuvette = 0.1 cm).

Results and Discussion

Changes in the 480–700 nm region in the spectrum of H_2TAPP solution upon addition of mercury(II)nitrate is presented in Fig. 1. Under the conditions of this titration, the freebase porphyrin exists in monomeric form. Resemblance of these changes to those obtained in the Hg^{2+}–H_2TPPS system indicates that the same type of product is obtained despite the peripheral positive charge. Here again, a set of well defined isosbestic points are observed at 556 nm and 490 nm, suggesting the absence of complex equilibria.

In order to understand the catalysis caused by mercury(II) ions in metal incorporation reaction [5, 6], a titration was carried out in the Soret region (400–450 nm), employing 10^{-6} *M* H_2TAPP. In this titration no clear isosbestic point was observed Moreover in addition to the expected Sorets due to freebase (412 nm) and the product mercuryporphy-

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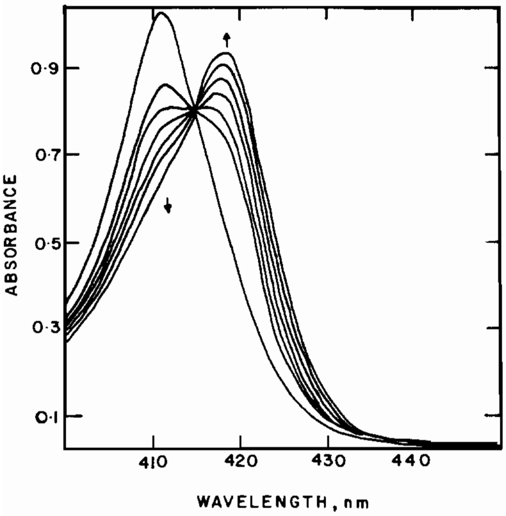

Fig. 3. Changes in the spectrum of H_2TAPP (2.5 × 10^{-7} *M*) during the titration with Hg^{2+} (path length of the cuvette = 10.0 cm).

rin, a third peak was noted. But when the titration was repeated employing the same concentration of H_2TAPP (5.12 × 10^{-5} *M*) as was employed before, the spectral changes were well defined with an isosbestic point at 421.5 nm (Fig. 2). Then titrations were carried out with H_2TAPP concentration in the range of 10^{-7} *M*. Spectral changes were well behaved with a clear cut isosbestic point at 415 nm (Fig. 3). The final product spectrum resembles that reported by Dorough *et al.* [7] for the normal 1:1 mercury(II)–tetraphenylporphyrin. Thus we treated this equilibrium observed in dilute porphyrin solutions as due to mono mercury–porphyrin. The same type of results were observed with H_2-TPPS also.

If the species observed in dilute porphyrin solutions are 1:1, (mercury:ligand), the species observed in concentrated porphyrin solutions cannot be 2:1 (mercury:ligand) as more ligand is available per metal ion in these solutions. Moreover, if 1:1 species at all possible, it should also be observed as a step in the formation of 2:1. Therefore we hypothesized the species observed in concentrated porphyrin solutions to be 3:2 (mercury:porphyrin) double sandwich type complexes. Mercury(II) is well known to adopt tetrahedral geometry in coordination. This 3:2 arrangement would perfectly satisfy such a geometry. Other porphyrins, such as octaethylporphyrin [8], are known to form such 3:2 species. The fact that H_2TPP formed a 2:1 rather than 3:2 (double sandwich) complex with mercury(II) was explained in terms of possible steric hindrance between phenyl rings of the porphyrins. But it is well known that H_2-TPPS and some of its metal complexes aggregate in water solutions. Thus the following two stoichiometries were assumed in the treatment of equilibria:

$$Hg^{2+} + H_2TAPP = HgTAPP + 2H^+ \text{ dilute solution} \quad (1)$$

$$(H_2TAPP \approx 10^{-7}\ M)$$

$$3Hg^{2+} + 2H_2TAPP = Hg_3(TAPP)_2 + 4H^+ \quad (2)$$

$$\text{Concentrated solution } (H_2TAPP \approx 10^{-5}\ M)$$

For reactions (1) and (2), the following equations can be derived:

$$K'_1 = (A_i - A_t)(A_t - A_f)^{-1} \times$$
$$\times\ [(Hg^{2+})\ \text{added} - (A_i - A_t)C_T\,(A_i - A_f)^{-1}]$$

$$\text{and } K_1 = K'_1(H^+)^2 \quad (3)$$

$$K'_2 = [(A_i - A_t)/4(A_t - A_f)^2)]\ [2(A_i - A_f)/C_T] \times$$
$$\times\ [(Hg^{2+})\ \text{added} - 3C_T(A_i - A_t)/2(A_i - A_f)]^{-3}$$

$$\text{and } K_2 = K'_1(H^+)^4 \quad (4)$$

where A_i, A'_t and A_f are absorbances of the solution at a constant wavelength initially, when varying amounts of Hg^{2+} are added and when $Hg_3(TAPP)_2$, (HgTAPP for eqn. (3)) is the only light absorbing species in solution, respectively; C_T is the total porphyrin concentration.

The equilibrium constants, $-\log K_1$, computed at 412 and 419 nm for 1:1 mercury-porphyrin complex are 8.34 ± 0.01 and 8.38 ± 0.01 respectively for peripherally positively charged porphyrin H_2-TAPP. Similar constants computed at 412 and 419 nm are 8.38 ± 0.08 and 8.38 ± 0.04 (for the peripherally negatively charged porphyrin H_2TPPS). The favorable comparison between these sets of equilibrium constants computed for the H_2TPPS and H_2TAPP rules out any notion of interference of either peripheral net charge or sulfonic acid groups in these systems.

The equilibrium constants computed for H_2-TPPS at 412, 433, 518 and 616 nm are 13.4 ± 0,1, 13.7 ± 0.2, 12.5 ± 0.3 and 12.8 ± 0.2 respectively. Similar constants for H_2TAPP, computed at 412, 433, 512 and 624 nm are 15.5 ± 0.3, 15.1 ± 0.4, 14.3 ± 0.4 and 13.8 ± 0.1, respectively. While for any system other than simple 1:1, this method of computation is not very sensitive or reliable, some broad conclusions can be made on these constants. Such large negative numbers indicate the general instability of the complex species. While H_2TPPS is known to aggregate, H_2TAPP does not aggregate under these conditions. Since in forming a double sandwich, any such aggregating or hydrophobic tendency would aid, it is not surprising that these constants are less negative for H_2TPPS system than for H_2TAPP system.

In conclusion, mercury(II) ions form weak complexes with water soluble porphyrins in ratio of 1:1 (metal to ligand) in lower porphyrin concentrations and in ratio of 3:2 (metal to ligand) in high porphyrin concentrations.

Acknowledgement

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References

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2 The following abbreviations for porphyrins employed in this study are used: H_2TPPS = the free base of tetra(*p*-sulfonatophenyl)porphyrin; H_2TAPP = free base of tetra(*p*-trimethylammoniumphenyl)porphyrin.
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