

## **TITRATION CALORIMETRIC INVESTIGATIONS ON THE INTERACTIONS OF Zn(II) PORPHYRIN COMPLEXES WITH PYRIDINE IN BENZENE AND CHLOROFORM AT 298.15 K**

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### **Abstract**

Titration calorimetry was used in a thermodynamic study on the interactions of pyridine with natural zinc(II) porphyrin derivatives in benzene and chloroform at 298.15 K. The ability of zinc porphyrins to coordinate to pyridine is higher in benzene than in chloroform and also depends on the molecular structure of the metalloporphyrin.

**Keywords:** complexation, titration calorimetry, Zn(II) porphyrin complexes with pyridine and benzene

### **Introduction**

Porphyryns and metalloporphyryns are important as a class of compounds of immense physical and chemical interest and for their crucial role in many biological processes. Metalloporphyryns are the prosthetic groups for a wide variety of proteins and enzymes involved in oxygen transport (myoglobin and hemoglobin), oxygen and peroxide activation (cytochrome P-450 and horseradish peroxidase), and electron transfer (cytochrome b) [1]. In all of the heme proteins investigated to date, the moiety is bound to the protein by at least one coordinate covalent bond between iron and the 'aromatic' nitrogen of a histidine residue of the protein. In some cases there are additional covalent or coordinate covalent linkages as in cytochromes b and c, but the iron-imidazole linkage is common to all those where axial ligands have been indentified [2]. Physicochemical and biological properties of naturally occurring heme proteins are controlled by various factors [3]. In heme proteins, there are several factors which may influence the function of the iron porphyrin, e.g. the oxidation state of the metal, the substituents on the porphyrin macrocycle, and the inner-sphere coordination. It has been observed in heme proteins that the aromatic moieties of amino acids such as phenylalanine, tyrosine and histidine are often oriented

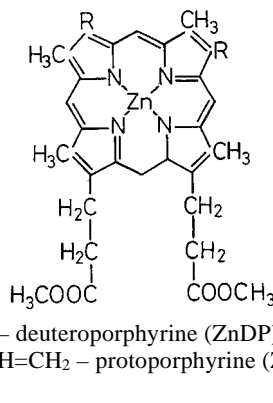
so as to be parallel to the porphyrin ring and sufficiently close to it that extensive overlap of their  $\Pi$ -orbitals with those of the porphyrin must occur [4, 5].

Recent studies indicated that  $\Pi$ -interactions with aromatic acceptors and donors can modulate the thermodynamic and kinetic parameters of axial ligations [6–10]. In this connection, study of the above-mentioned structural and solvation factors and their influence on the coordinating properties of natural metalloporphyrins in relation to electron-donor or -acceptor molecular ligands is of great importance.

Accordingly, our aim was to study the interactions of natural zinc(II) porphyrins (Fig. 1) with an electron-donor ligand (pyridine) and an aromatic  $\Pi$ -donor molecule (benzene) and to establish the influence of structural and solvation factors on the thermodynamic characteristics of axial pyridine coordination in different solvents (benzene and chloroform).

## Materials and methods

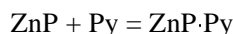
The complexes of zinc(II) with protoporphyrin IX dimethyl ester (ZnPP), hematoporphyrin IX tetramethyl ester (ZnHP), deuteroporphyrin IX dimethyl ester (ZnDP) and mesoporphyrin IX dimethyl ester (ZnMP) were prepared and purified according to literature methods [11]. The solvents benzene, chloroform and pyridine (Sigma) were distilled and dried over a 4A molecular sieve. Purity was checked chromatographically and found to be 99.98% for benzene and pyridine and 99.95 % for chloroform. The water contents in the solvents, as determined by the Fisher method, were below 0.01%. Chloroform was stabilized with amylene (2-methyl-2-butene), which is inert to these metalloporphyrins (in a proportion of 1:1000).



**Fig. 1** Zn(II) porphyrines.  $R=D$  – deuteroporphyrine (ZnDP);  $R=-CH_2-CH_3$  – mesoporphyrine (ZnMP);  $R=-CH=CH_2$  – protoporphyrine (ZnPP);  $R=-CH-CH_3$  – hematoporphyrine (ZnHP)

The thermodynamic parameters of the interactions of pyridine with zinc(II) porphyrins (ZnP) in benzene and chloroform at 298.15 K were examined by a microcalorimetric titration method. A titration calorimeter of sensitivity  $64 \text{ V W}^{-1}$ , equipped with a calorimetric vessel  $10 \text{ cm}^3$  in volume, was used for the measurements. The titrant,  $0.19\text{--}0.25 \text{ mol dm}^{-3}$  pyridine (Py), was microdosed into the calorimetric vessel at uniform intervals. The number of doses in one experiment was 6–17. The titra-

tion process was stopped when the excess of the titrant in the solution was not less than 10 mol for 1 mol of ZnP. The initial concentration of the ZnP solutions was in the range  $(0.3\text{--}2.5)\cdot 10^{-3}$  mol dm<sup>-3</sup> and was checked spectroscopically. The results obtained indicate that in all cases pyridine interacts with ZnP to form a 1:1 complex:



The complex formation equilibrium constant  $K_c$  can be expressed [12] as

$$K_c = c(\text{ZnP}\cdot\text{Py})c^0 / c(\text{ZnP})c(\text{Py}) \quad (1)$$

or

$$K_c = c(\text{ZnP}\cdot\text{Py})_n c^0 \{ [c^0(\text{ZnP})_n - c(\text{ZnP}\cdot\text{Py})_n] [c^0(\text{Py})_n - c(\text{ZnP}\cdot\text{Py})_n] \} \quad (2)$$

where  $c(\text{ZnP}\cdot\text{Py})_n$  is the concentration of complex upon addition of  $n$  doses of the ligand pyridine;  $c(\text{ZnP})_n$  denotes the total concentration of  $c(\text{ZnP}) + c(\text{ZnP}\cdot\text{Py})$  following the  $n$ -th dose of the ligand solution;  $c(\text{Py})_n$  is the sum of the bound and non-bound ligand concentrations following the  $n$ -th dose; and  $c^0 = 1$  mol dm<sup>-3</sup>.

The relation between the sum  $Q_n$  of the heats involved, following the  $n$ -th titration step, and the molar enthalpy  $\Delta H_m$  of the process can be expressed as

$$Q_n = \Delta H_m V_n c(\text{ZnP}\cdot\text{Py})_n \quad (3)$$

where  $V_n$  is the total volume of the reaction mixture upon addition of the  $n$ -th dose.

After substituting (3) into (2), we obtain

$$1/K_c = c(\text{ZnP})_n c(\text{Py})_n \Delta H_m V_n / Q_n c^0 - c(\text{ZnP})_n / c^0 - c(\text{Py})_n / c^0 + Q_n / \Delta H_m V_n \quad (4)$$

The algorithm of the least square sum method was used to determine  $\Delta H_m$ ,  $K_c$  and then the molar entropy  $\Delta S_m$  of the process studied.

## Results and discussion

The experimental data are presented in Table 1, and the  $\Delta H_m$ ,  $K_c$  and  $\Delta S_m$  values calculated from them in Table 2. Inspection of the data in Table 2 demonstrates that a) the enthalpy and entropy of the pyridine – ZnP interactions in benzene are always negative; b)  $\Delta H_m$  is increasingly negative in the sequence ZnHP < ZnDP < ZnMP < ZnPP. The interaction of pyridine with ZnPP shows the largest entropy decrease ( $-81.6$  J mol<sup>-1</sup> K<sup>-1</sup>). The interaction with ZnHP in chloroform is characterized by the lowest  $K_c$ . A possible reason for the low coordinating ability of ZnHP in relation to pyridine in chloroform is the specific solvation of the oxygen-containing peripheral substituents of porphyrin due to the formation of H-bonds with chloroform molecules. The ZnHP molecule has four ester groups as peripheral substituents, while the other ZnP contain dimethyl esters, so they demonstrate a lesser degree of specific chloroform solvation effects. The CH<sub>3</sub>(OCH<sub>3</sub>)CH substituent in hematoporphyrin demonstrates

**Table 1** Experimental titration results ( $T=298.15$  K) for the reaction of Zn(II) porphyrin derivatives with pyridine in the solvents benzene and chloroform

Reaction: ZnPP(sol)+Py(sol)=ZnPP·Py(sol) <sup>a</sup>		Reaction: ZnMP(sol)+Py(sol)=ZnMP·Py(sol) <sup>a</sup>	
Solvent: C <sub>6</sub> H <sub>6</sub>		Solvent: C <sub>6</sub> H <sub>6</sub>	
$c(\text{ZnPP})_0=0.351 \cdot 10^{-3} \text{ mol dm}^{-3 \text{ b}}$		$c(\text{ZnMP})_0=0.678 \cdot 10^{-3} \text{ mol dm}^{-3 \text{ b}}$	
$c(\text{Py})_0=0.192 \cdot 10^{-3} \text{ mol dm}^{-3 \text{ b}}$		$c(\text{Py})_0=0.192 \cdot 10^{-3} \text{ mol dm}^{-3 \text{ b}}$	
$V_0/10^{-3} \text{ dm}^3 \text{ c}$	$V/10^{-3} \text{ dm}^3 \text{ d}$	$V_0/10^{-3} \text{ dm}^3 \text{ c}$	$V/10^{-3} \text{ dm}^3 \text{ d}$
$Q_n/J^e$		$Q_n/J^e$	
8.6653	8.5987	8.3015	8.3836
0.0255	0.0204	0.00765	0.00765
0.0253	0.0270	0.0392	0.0394
0.0506	0.0497	0.0767	0.0765
0.0707	0.0684	0.1062	0.1061
0.0838	0.0816	0.1270	0.1271
0.0932	0.0912	0.1417	0.1417
0.0997	0.0976	0.1520	0.1527
0.1053	0.1030	0.1616	0.1617
0.1091	0.1076	0.1688	0.1688
0.1129	0.1108	0.1741	0.1741
		0.1780	0.1785
			0.1825

Table 1 Continued

Reaction: ZnDP(sol)+Py(sol)=ZnDP·Py(sol) <sup>a</sup>		Reaction: ZnHP(sol)+Py(sol)=ZnHP·Py(sol) <sup>a</sup>	
Solvent: C <sub>6</sub> H <sub>6</sub>		Solvent: C <sub>6</sub> H <sub>6</sub>	
c(ZnDP) <sub>0</sub> =0.444·10 <sup>-3</sup> mol dm <sup>-3</sup> <sup>b</sup>		c(ZnHP) <sub>0</sub> =1.194·10 <sup>-3</sup> mol dm <sup>-3</sup> <sup>b</sup>	
c(Py) <sub>0</sub> =0.192·10 <sup>-3</sup> mol dm <sup>-3</sup> <sup>b</sup>		c(Py) <sub>0</sub> =0.192·10 <sup>-3</sup> mol dm <sup>-3</sup> <sup>b</sup>	
	V <sub>0</sub> /10 <sup>-3</sup> dm <sup>3</sup> <sup>c</sup>		V <sub>0</sub> /10 <sup>-3</sup> dm <sup>3</sup> <sup>c</sup>
9.8829	8.7868	9.5131	8.6949
0.0153	V/10 <sup>-3</sup> dm <sup>3</sup> <sup>d</sup>	0.0051	V/10 <sup>-3</sup> dm <sup>3</sup> <sup>d</sup>
	0.0051		0.0153
	Q <sub>n</sub> /J <sup>e</sup>		Q <sub>n</sub> /J <sup>e</sup>
0.0779	0.0298	0.0259	0.0940
0.1240	0.0574	0.0497	0.1790
0.1335	0.0816	0.0701	0.2514
0.1389	0.1011	0.0852	0.3137
0.1419	0.1090	0.0941	0.3580
0.1444	0.1151	0.1016	0.3941
	0.1204	0.1077	0.4221
	0.1238	0.1136	0.4459
	0.1259	0.1184	0.4635
	0.1280	0.1223	0.4785
			0.4917
			0.5003
			0.5124
			0.5207
			0.5276
			0.5022
			0.5088
			0.5141
			0.4669
			0.4569
			0.4425
			0.4271
			0.4065
			0.3847
			0.3544
			0.3175
			0.2625
			0.1845
			0.0935
			0.0153
			8.2890

Table 1 Continued

Reaction: ZnPP(sol)+Py(sol)=ZnPP·Py(sol) <sup>a</sup>		Reaction: ZnMP(sol)+Py(sol)=ZnMP·Py(sol) <sup>a</sup>	
Solvent: CHCl <sub>3</sub>		Solvent: CHCl <sub>3</sub>	
c(ZnPP) <sub>0</sub> =1.002·10 <sup>-3</sup> mol dm <sup>-3</sup> <sup>b</sup>		c(ZnMP) <sub>0</sub> =1.659·10 <sup>-3</sup> mol dm <sup>-3</sup> <sup>b</sup>	
c(Py) <sub>0</sub> =0.250·10 <sup>-3</sup> mol dm <sup>-3</sup> <sup>b</sup>		c(Py) <sub>0</sub> =0.250·10 <sup>-3</sup> mol dm <sup>-3</sup> <sup>b</sup>	
0.250	0.125	0.125	
	V <sub>0</sub> /10 <sup>-3</sup> dm <sup>3</sup> <sup>c</sup>		V <sub>0</sub> /10 <sup>-3</sup> dm <sup>3</sup> <sup>c</sup>
8.8703	9.3903	9.1804	9.5036
	V/10 <sup>-3</sup> dm <sup>3</sup> <sup>d</sup>		V/10 <sup>-3</sup> dm <sup>3</sup> <sup>d</sup>
0.0204	0.0204	0.0204	0.0255
	Q <sub>n</sub> /J <sup>e</sup>		Q <sub>n</sub> /J <sup>e</sup>
0.0919	0.0460	0.1112	0.1076
0.1435	0.0862	0.2214	0.2096
0.1684	0.1163	0.2936	0.2783
0.1865	0.1402	0.3325	0.3172
0.1983	0.1595	0.3538	0.3448
0.2054	0.1727	0.3708	0.3642
0.2106	0.1818	0.3856	0.3806
0.2117	0.1908	0.3983	0.3946
	0.1984	0.4107	0.4071
		0.4204	0.4194
		0.4291	0.4016
			8.1165
			0.0255
			0.1035
			0.2036
			0.2744
			0.3125
			0.3477
			0.3582
			0.3786
			0.3901
			0.3999
			0.4016

Table 1 Continued

Reaction: ZnDP(sol)+Py(sol)=ZnDP·Py(sol) <sup>a</sup>		Reaction: ZnHP(sol)+Py(sol)=ZnHP·Py(sol) <sup>a</sup>	
Solvent: CHCl <sub>3</sub>		Solvent: CHCl <sub>3</sub>	
c(ZnDP) <sub>0</sub> =2.500·10 <sup>-3</sup> mol dm <sup>-3</sup> <sup>b</sup>		c(ZnHP) <sub>0</sub> =1.396·10 <sup>-3</sup> mol dm <sup>-3</sup> <sup>b</sup>	
c(Py) <sub>0</sub> =0.250·10 <sup>-3</sup> mol dm <sup>-3</sup> <sup>b</sup>		c(Py) <sub>0</sub> =0.250·10 <sup>-3</sup> mol dm <sup>-3</sup> <sup>b</sup>	
	V <sub>0</sub> /10 <sup>-3</sup> dm <sup>3</sup> <sup>c</sup>		V <sub>0</sub> /10 <sup>-3</sup> dm <sup>3</sup> <sup>c</sup>
7.7390	7.5835	7.2246	9.3409
	V/10 <sup>-3</sup> dm <sup>3</sup> <sup>d</sup>		V/10 <sup>-3</sup> dm <sup>3</sup> <sup>d</sup>
0.0204	0.0204	0.0204	0.0204
	Q <sub>n</sub> /J <sup>e</sup>		Q <sub>n</sub> /J <sup>e</sup>
0.1276	0.1319	0.1392	0.0654
0.2461	0.2578	0.2688	0.1157
0.3557	0.3519	0.3782	0.1549
0.4308	0.4152	0.4363	0.1830
0.4758	0.4600	0.4722	0.2030
0.5105	0.4865	0.4982	0.2196
0.5306	0.5079	0.5183	0.2325
0.5424	0.5259	0.5371	0.2421
0.5532	0.5411	0.5539	0.2505
0.5609	0.5553	0.2504	0.2571
0.5661	0.5682	0.2597	0.2634
0.5702		0.2667	0.2788

<sup>a</sup> ZnPP denotes complexes of zinc(II) with protoporphyrin IX-dimethyl ester, ZnMP denotes complexes of zinc(II) with mesoporphyrin IX-dimethyl ester,<sup>b</sup> ZnDP denotes complexes of zinc(II) with deuteroporphyrin IX-dimethyl ester, ZnHP denotes complexes of zinc(II) with hematoporphyrin IX-dimethyl ester<sup>c</sup> Initial concentration<sup>d</sup> Initial volume of ZnPP, ZnMP, ZnDP or ZnHP<sup>e</sup> Average microdose volume of Py(sol)<sup>f</sup> Sum of the enthalpy change for the *n*<sup>th</sup> titration step

an overall negative electron effect in relation to the macroring. The formation of H-bonds with solvent molecules must weaken the electron-acceptor properties of the given substituent, which in turn leads to a strengthening ZnP interaction and weaker coordinating properties of ZnHP. Further, chloroform molecules H-bonded to peripheral groups can present steric obstacles to the coordination of pyridine molecules.

**Table 2** Equilibrium constants  $K_c$ , molar enthalpies  $\Delta H_m$  and molar entropies  $\Delta S_m$  for the process of interactions of zinc(II) porphyrins with pyridine in benzene and chloroform at 298.15 K

System	$\Delta H_m /$ kJ mol <sup>-1</sup>	$K_c$	$\Delta S_m /$ J mol <sup>-1</sup> K <sup>-1</sup>
ZnPP·Py(C <sub>6</sub> H <sub>6</sub> )	-45.7±0.8	5795±310	-81±3
ZnMP·Py(C <sub>6</sub> H <sub>6</sub> )	-35.8±0.4	5586±339	-48±2
ZnDP·Py(C <sub>6</sub> H <sub>6</sub> )	-33.6±0.4	17646±1637	-31±3
ZnHP·Py(C <sub>6</sub> H <sub>6</sub> )	-33.1±0.4	4694±391	-41±3
ZnDP·Py(CHCl <sub>3</sub> )	-32.1±0.3	2592±204	-42±2
ZnMP·Py(CHCl <sub>3</sub> )	-29.2±0.3	2590±143	-33±2
ZnPP·Py(CHCl <sub>3</sub> )	-25.4±0.4	3267±220	-18±2
ZnHP·Py(CHCl <sub>3</sub> )	-24.6±0.3	1136±44	-24±2

Analysis of the results obtained demonstrates that the process of axial pyridine coordination for all the natural ZnP under study is more exothermic in benzene than in chloroform. A similar dependence of thermodynamic characteristics on the nature of solvent was earlier reported for the interaction of Fe(II) protoporphyrin with 4-methylpyridine and a number of metalloderivatives of tetraphenylporphyrin with pyridine [13], which was due to the better solvation ability of chloroform in comparison with that of benzene.

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