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Thermodynamic Study on Reaction of Tetra Sulfona to Phenyl Porphyrin Iron (II) Complex With Different Nitrogenous Ligands

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A B S T R A C T

The binding characteristics of number of axial aliphatic amines ligands were studied with Fe(ll)TPPS$_4$ complex in aqueous solutions at hiqh PHs > 12.5 . All formed low spin octahedral complexes . Electronic absorption, ΔH, ΔG, and ΔS of these complexes have been reported and Calculated . The Path way for the axial ligation on addition of ligand to Fe(ll)TPPS$_4$ is shown in one step . Hill Plots used to obtain the formation constants (K$_F$) and (n) number of axial ligands bonded to the iron(ll) ion . It has been found low values of the K$_F$ for these ligands comparing to those recorded in organic solvents may be due to the polar solvent, and these values (K$_F$) more higher than that recorded for aromatic amine with the same complex and solvents due to steric effect of the size of porphyrin ring.

Introduction :

The studying of the chemistry of Iron (ll) porphyrins in aqueous solution is of interest to chemists and biochemists for many reasons, three of which are :

1. Iron prophyrins, in particular protoporphyrin IX iron is the prosthetic group of a large number of metalloproteins[1], hence water soluble haems are useful in modeling its chemistry.

2. Because many natural products (e.g. chlorophylls, cytochromes and vitamin B12) contain these molecules [2] .

3. Iron porphyrins because of their role as nature's catalysis [1] may well have industrial applications. Many workers[2-4] have studied the binding of axial ligands to four coordinate haem centers, they found no evidence for step – wise addition of the ligand and the formation of an octahydral complex was observed . They[5,6] found that the log B$_2$ increased (its binding constant) with increasing basicity of the pyridine ligand, where, K$_2$>> K$_1$, B$_2$ = K$_2$. K$_1$

$$Fe\ (ll)P + 2L \longrightarrow Fe(ll)P(L)_2 \quad . (eq1)$$

A condition where δ-effects predominate this for diacetyl deuteron porphyrin . Brault et al [7] have found slightly higher affinities of Fe (ll) TPP for imidazole .

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When compared with that pyridine, they found the binding for both ligands occurs in two steps (eq.2).

$$Fe\ (ll)\ TPP+L \xrightarrow{K1} Fe(ll)TPPL + L \xrightarrow{K2} Fe(ll)TPPL_2$$
.(eq.2)
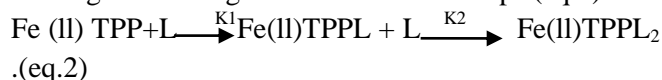
Other workers[8] have studied the binding of nitrogen ligands to the Fe(ll)PP 1X in aqueous solvent at high PH . they found the stability constant for Fe(ll)PP 1X complexes in alkali media is less than that for Fe(ll)TPP complexes (e.g.imidazole,pyridine) in Organic solvents.

In this work was studing the stability constant of aliphatic amines with different number nitrogen atoms addition to its thermodynamic parameters to water soluble haem Fe(ll)TPPS$_4$ and to compare them with others aromatic amines and soluble haem [9,10] .

Experimental :

Tetra (sulphophenyl) porphine iron(ll) was prepared by reducing μ-OXO bis tetra (sulphophenyl) porphine iron (lll), O (TPPS$_4$ Fe(lll))$_2$ at high PHs of 12.5 solution with sodium dithionite . O (TPPS$_4$ Fe(lll))$_2$ was prepared as previously described [11].

Elemental analysis (C.H.N) for TPP (M.Wt = 615 g/mol = C$_{44}$H$_{30}$N$_4$), C % = 85.85 (84.45), H % = 4.88 (5.04) , N % = 9.10 (8.97) . for TPPS$_4$ (M.Wt = 938 g/mol = C$_{44}$H$_{34}$N$_4$O$_{12}$S$_4$) C % = 56.29 (55.91), H % = 3.62 (3.70), N % = 5.97 (5.92), S % = 13.65 (13.41), O % = 20 . 47 (20.50).

The electronic absorption spectra were recorded on solutions that had been freshly prepared in a three-

necked flask. One neck allowed N_2 in and out, another the samples to be removed, the third was used for a PH electrode. 50 ml of TPPS Fe(lll), solutions of appropriate concentration were used . The concentration of TPPS Fe(ll) solution was 5.65×10^{-5} M prepared at PH 12.5 in buffer of KCl + NaOH 0.1 M and adjusted to give a PH around 12.5 3ml quartz cells were used, The spectra were obtained using 1 cm path length cells containing 2.5 ml of solution.The quartz cells are sealed under an N_2 atmosphere, and measured using a lambda 5G spectrophotometer. Spectrophotometric titrations on the addition of the ligand to the Fe (ll) $TPPS_4$ solutions were carried out, (using an air protected syringe), in a covette closed by a Teflon cap,a minimum of 2 minutes of vigorous shaking was necessary to ensure establishment of the equilibrium before the spectrum was taken . Every titration was repeated three time to get the average of the stability constant, and studied at different wave lengths and temperatures.

Materials : All the nitrogenous ligands were purchased from Aldrich as listed in table -1 .

Results and Discussion :

1 . Visible spectra:

On addition of excess of the nitrogen ligands to the solutions of $TPPS_4$ Fe(II), a dramatic change in the spectra results due to formation of complexes at high PHS and gives three bands in their spectra, they are summarized in Table- 2. The spectra of Fe (II) $TPPS_4$ solutions with these strong ligands that are characterized by a set of three bands, α, β and ɣ bands and appear respectively from the longer to shorter wavelength. The visible absorption spectrum of these complexes are sharp and its assigned of low spin complexes, this sharpening results from the change of the polymer to monomer breakdown of O-(Fe(ll) TPPS)$_2$ or from high spin to low spin iron(ll) complexes [11,12]. In this work it was observed that the soret band and other visible bands of iron (II) sulphonated and non-sulphonated porphyrins were shifted from the longer to the shorter wavelength upon addition of the ligands. It has been reported that the shift of the soret band of Fe(ll)PPIX-amines to the longer wave length as a result of the π- electron density of the metal t_{2g} orbitals moving to wards the periphery of the planar porphyrin nucleus but with saturated ligands such those in this work, the metal t_{2g} orbitals (dxz,dyz) are involved in π-bonding with these

ligands and this causes a decrease in the overlapping of metal t_{2g} orbital with π-orbitals of the porphyrin ring via the nitrogen atoms, this causes a shift of the soret band to shorter wave length [13,14].

2 . Spectrophotometric titrations :

The reaction of nitrogenous ligands with Fe(ll) $TPPS_4$ solutions at high PH in aqueous solvent makes spectral changes .Well defined isosbestic points are observed, typical spectrophotometric titration are presented in figures 1,2. These reactions are rapid and quickly reach a point at which no further change in absorbance occurs suggesting strong binding constants. These changes were similar for all these nitrogen ligands with different iron (II) porphyrin complexes [15 -21] see table 3.

Hill plots [22] were constructed to analysis these data, to measure the K_{eq} at different wave length and temperature ranges (20-30) C^o .

Log $= A - A_o / A_\infty$ $-$ A $=$ log K $+$ nlog(L)……………(eq.3)

ΔH,Δ G and ΔS were calculated for these reactions from (eq.4 - eq.7) and are presented in table-4. The Fe (II) $TPPS_4$ bind two ligand molecules from slope (n >1.9) and the resulting complexes are low spin. Stability constants of Fe (II) $TPPS_4$ with these amines at similar temperature slightly higher values than for the Fe (II) $TPPS_4$ and Fe (ll) PPIX with the aromatic ligands [8].

When plots of log (A - A$_o$) (A$_\infty$- A) vs. log (L)[21]. A is the absorbance at the wave length of study of mixed species. A$_o$ is the absorbance of Fe (II) $TPPS_4$ in the absence of L and A$_\infty$ is the absorbance in the presence of a large excess of L, were constructed, straight lines were obtained, see figures(3, 4 a b, 5 a b) .

H $= 19.14$ T_1 T_2 (log K_2 $-$ log K_1)/ (T_2 $-T_1$)…… Kcal/mol.K   ……(eq.4)Δ

Or

H $= 4.576$ $T_1 T_2$(log K_2 $-$ log K_1)(T_2-T_1)……cal/mol.K ….(eq.5)Δ

G $=$ $-$ 4.576 T log Keq ……… cal/mol.K ………(eq.6)Δ

S $=$ ΔH $-$ ΔG/T ……….… cal/mol.K ……………(eq.7)Δ

Log B_2 (log k$_{eq}$) is estimated from the intercept of the portion of the graph, which as slope of 2 (or more/ less). The value of (n) is the slope which is known as the Hill constant [22], this value if less or more than two results from water solvent effect[17-20]

(polar solvent) it did not greatly affect the log K_{eq} values .

It has been found that the log k_{eq} values increase with increasing the number of nitrogen atoms of amines except the EDTA decrease it was unstable and less soluble in water and these values decrease with increasing the temperature of reaction .Aliphatic amine were found in this study form complexes with Fe(ll)TPPS$_4$ more stable and hiqh values of log K_{eq}, we think that due to the less steric effect of porphyrin ring size [9] .

The variation in ΔH from (- 19 . 37) to (- 160.57) Kcal/mole reflects an increase in the Fe(ll) – nitrogen ligand bond energy with increasing the long of aliphatic amine chain and electronegatively on the nitrogen atoms of ligands . These values (ΔH, log K_{eq}) were found hiqher than that recorded to the Fe(ll) TNPS$_4$, Fe(ll) TPPS$_4$ complexes with aromatic amines [10], that may be due to the good σ -donor might be expected to be a poor π – accepter   and will approach the haem closely.

Conclusions:

In this work the stability characteristics of numbers of aliphatic amines were studied with Fe(ll) TPPS$_4$ in aqueous solutions. All found form low spin octahedral complexes .The visible spectra of these complexes have been characterised in general by a set three bands which shift to shorter wave length compared to the unligated parent complexes.

Stability constants for these complexes with these amines have been calculated at two temperatures for Fe(II) TPPS$_4$, from Hill plots. ΔH, ΔG and ΔS have been calculated by using (eq.4). Hill plots [22] have been used to obtain the K_{eq} and Hill constants (n).The low values of the K_{eq} for these ligands in this study in aqueous media have been explained as follows.

a.The polar solvent might make solute. Solvent interactions and lower the both values [23].

b. The polymerization and aggregation of this type of porphyrins (Fe(ll) TPPS) complexes in aqueous solution will lower the values of K_{eq} [24].

c. The values of (n), log K_{eq} and ΔH were found increas by increasing the molecular weight, number of nitrogen a toms and sigma (σ) donor of ligands

Table – 1 : **Nitrogenous ligands used in this study**

NO	Amine	Formula	M.Wt (g/mol)	Purity %
1	B-Alanine (L-1)	$NH_2 (CH_2)_2COOH$	89.09	99.0
2	Ethylene di amine (L-2)	$NH_2 (CH_2)_2NH_2$	60.00 S.P = (0.89)	97.0
3	Di ethylene tri amine (L-3)	$NH_2 (CH_2CH_2)_2 NH NH_2$	103.17 S.P = (0.95)	99.0
4	Tri ethylene tetra amine (L-4)	$NH_2 (CH_2CH_2)_3 NH NH NH_2$	146.23 S.P = (0.982)	97.0
5	Tetra ethylene penta amine (L-5)	$NH_2 (CH_2CH_2)_4 (NH)_3 NH_2$	189.30 S.P = (0.998)	98.0
6	Penta ethylene hexa amine (L-6)	$NH_2 (CH_2CH_2)_5 (NH)_4 NH_2$	232.37 S.P = (0.95)	98.0
7	EDTA Na$_2$ .2H$_2$O (L-7)	$C_{10}H_{14}N_2 O_8Na_2.2H_2O$	372.25	86.80
8	Imadizole (L-8)	$C_3H_4N_2$	68.06	88.50

Table – 2 : Electronic absorption of Fe(ll)TPPS4 with amines at 20Co in aqueous solutions (PH = 12.5)

NO	Compounds	(nm)γ	β(nm)	α(nm)
1	FeTPPS$_4$ (PH=2.0)	394	528	.....
2	FeTPPS$_4$ (PH=12.0)	415	566	606
3	Fe(ll)TPPS$_4$	436	567	607
4	Fe(ll)TPPS$_4$ (PH=12.8)	439	568	608 [10]
5	Fe(ll)TPPS$_4$ + L - 1	426	529	562
6	Fe(ll)TPPS$_4$ + L - 2	425	530	562
7	Fe(ll)TPPS$_4$ + L - 3	426	530	562
8	Fe(ll)TPPS$_4$ + L - 4	425	530	562
9	Fe(ll)TPPS$_4$ + L - 5	426	529	562
10	Fe(ll)TPPS$_4$ + L - 6	425	530	561
11	Fe(ll)TPPS$_4$ + L - 7	524	529	562
12	Fe(ll)TPPS$_4$ + L - 8	427	531	560

Table–3: Shows the spectrophotometric titration analysis of all figures in this study.

NO	Donor	Slope±0.1n		Log K_{eq}±0.15 [M^{-2}]		Log $_D$±0.01 [M]	
		293K	303K	293K	303K	293K	303K
1	Beta – alanine	2.108	1.908	5.013	4.638	0.1995	0.2156
2	Ethlene di amine	2.384	2.241	6.721	6.342	0.1488	0.1577
3	Di ethylene tri amine	2.171	2.152	6.894	6.457	0.1450	0.1549

	4	5	6	7	8	9	10	11	12
Donor	Tri ethylene tetra amine	Tetra ethylene penta amine	Penta ethylene hexa amine	Imadizol	EDTANa$_2$ H$_2$O	3,4 – di methyl pyridine *	Pyridine *	Pyridine **	3- amino methyl pyridine
	2.466	2.503	2.362	2.124	2.135	1.73 (288k)	1.87 (288k)	1.66 (288k)	1.97 (288k)
	2.152	2.151	2.267	2.088	2.228	1.50	1.82		1.92
	7.668	8.422	8.711	7.327	3.923	6.30	6.27	6.50	5.80
	7.334	7.477	7.792	6.973	3.809	6.16	6.10		5.60
	0.1304	0.1187	0.1148	0.1365	0.2549	......	......		
	0.1363	0.1337	0.1283	0.1434	0.2625	....	......		

*Ref = [9], ** Fe(ll)TNPS [10]

Table –4 : Thermodynamic parameters for amines binding in aqueous solutions of Fe(ll)TPPS4.

NO	Donor	ΔH Kcal/mole.K	ΔG Kcal/mole.K	ΔS Cal/mole . K	
1	Beta – alanine	-63.700	-28.10	-121.50	293K
			-26.90	-121.45	303K
2	Ethlene di amine	-64.400	-37.69	-91.160	293K
			-36.78	-19.150	303K
3	Di ethylene tri amine	-74.260	-38.66	-121.50	293K
			-37.45	-121.48	303K
4	Tri ethylene tetra amine	-56.750	-31.88	-84.88	293K
			-31.53	-83.23	303K
5	Tetra ethylene penta amine	-160.57	-47.23	-386.8	293K
			-43.36	-386.8	303K
6	Penta ethylene hexa amine	-156.16	-48.85	-366.2	293K
			-45.19	-366.2	303K
7	Imadizol	-60.150	-41.10	-65.02	293K
			-40.44	-65.05	303K
8	EDTANa$_2$H$_2$O	-19.370	-22.00	8.980	293K
			-22.10	9.010	303K
9	3,4 – di methyl pyridine*	-10.50	-8.70	-6.30	
10	Pyridine**	-11.40	-8.50	-10.0	

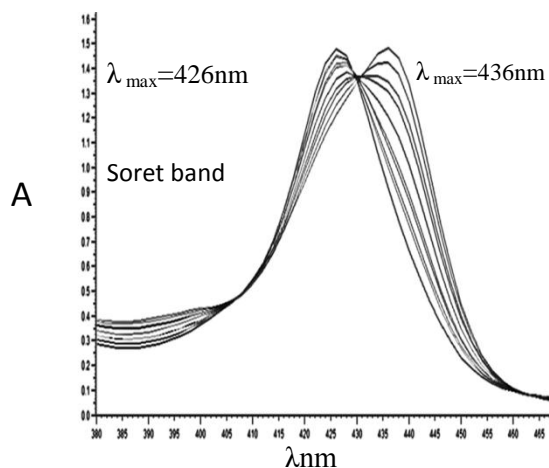*Fe(ll)TPPS (288K), ** Fe(ll)TNPS (288K) [10].

Figure – 1 : The soret band region of the titration Fe(ll) TPPS$_4$ with β – alanine [1M] at 293 K, PH = 12.5 .
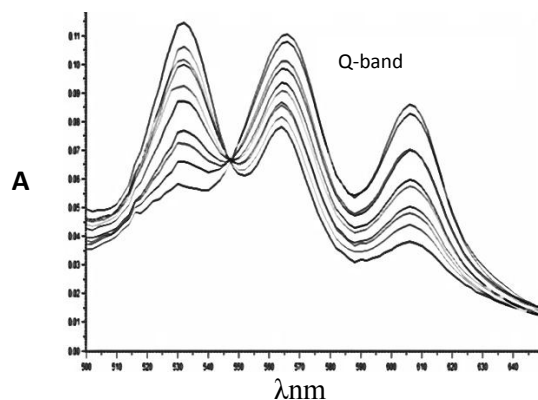

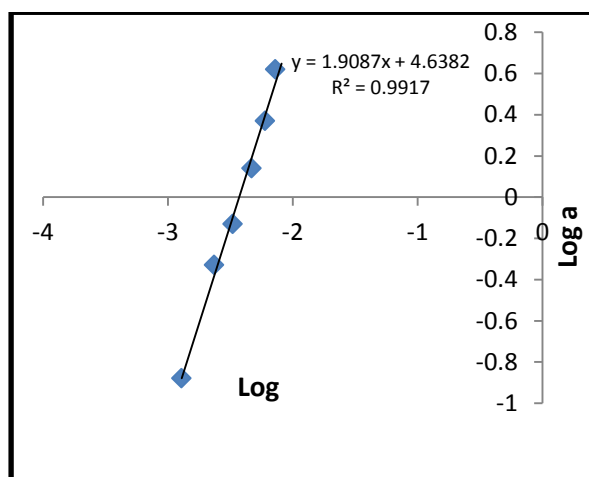**Figure -2 : The visible region of the titration Fe(ll)TPPS4 with β – alanine [1M] at 293 K, PH = 12.5 .**

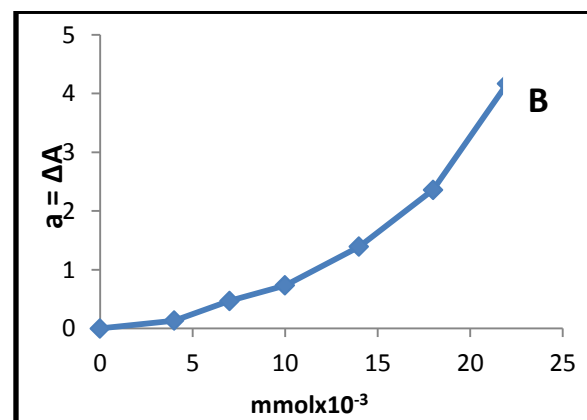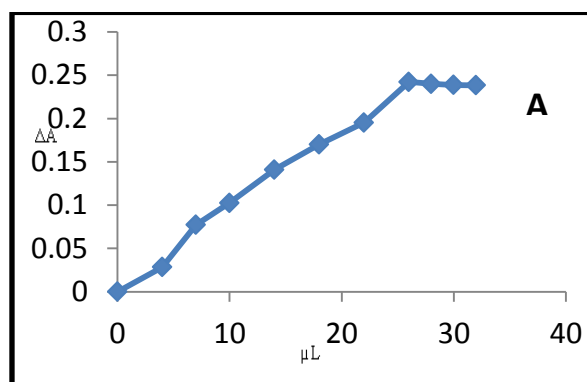**Figure – 3 : Hill plot for Fe(ll)TPPS4 (β – alanine)2 at 303 K .**

Figure – 4 : (a) Shows the relation between . μ L (microliter) and Δ A at 293 K.(b) between mmol and Δ A / ΔA∞ at 303K .

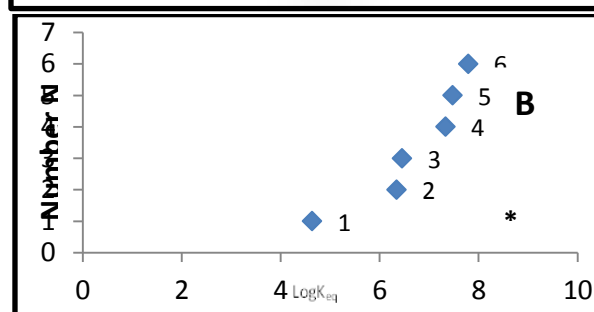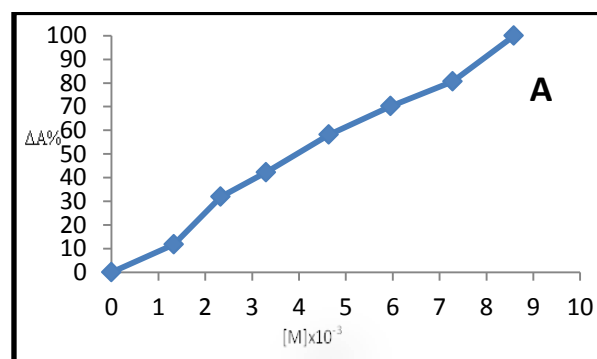**Figure – 5 : (a) The relation between [M] of ligand and ΔA% at 303K . (b) between log Keq and number of N atom at 303 K .**

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دراسة ثرموديناميكية تفاعل معقد رباعي سلفوفنيل بورفرين حديد ثنائي مع ليكاندات نايتروجينية مختلفة

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الخلاصة :

تم دراسة ارتباط عدد من ليكاندات الامينات الاليفاتية مع رباعي سلفوفنيل بورفرين حديد ثنائي في وسط قاعدي دالته الحامضية اكثر من 12.5، جميع التفاعلات تكون معقدات ثماني السطوح برم واطئ. الاطياف الالكترونية، ΔH، ΔG، ΔS، تم حسابها وتتم هذه التفاعلات بخطوه واحده. استخدم

مخطط هيل لحساب ثابت الاستقرار وعدد اليكاندات المتعاضدة (n) مع ايون الحديد الثنائي حيث وجدت قيم K_f واطئة مقارنة لنفس المعقدات في المذيبات العضوية تبعاً لقطبية المذيب لكن هذه القيم (K_f) اكثر من التي سجلت لليكاندات امينية اورماتية في وسط مائي نتيجة لتأثير الاعاقة لحلقة البورفرين.

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