

Determination of Entropy and Enthalpy values of Metal Gallic Acid Complexes and their Comparison with Iron Gallate

¹FOUZIA SULTANA, ²ZAHIDA MAQSOOD AND ²S. ARIF KAZMI

¹*Institute of Biochemistry, Baluchistan University, Quetta, Pakistan*

²*Department of Chemistry, University of Karachi, Karachi, Pakistan*

(Received 20th April, 1995, revised 12th August, 1995)

Summary: The entropy and enthalpy values of complex formation between 3,4,5 trihydroxybenzoic acid and Cu(II), Cr(II), Mn(II), Mg(II) and Ca(II) were determined and compared with the iron gallic acid complexes, they were found to be comparable.

It was also found that they show very large entropy values. When those values were compared with other complexes of the same nature from literature, following points were noteworthy.

1. Monodentate ligands do not show any drastic entropy change with trivalent metals as compared to divalent metals.

2. Polydentate ligands show very high entropy values with tripositive metal as compared to dipositive metals.

3. Non transition metals show low entropy values with chelating agents as compared to transition metals.

Introduction

While iron is an essential trace element, its excess is toxic. A number of endogenous as well as exogenous molecules have affinity for iron and are known to chelate iron in a biological environment. A number of drugs function by modulating the concentration of iron in biological fluids and excess of toxic iron in iron overload patients is removed by administration of synthetic or natural iron chelators [1-5]. How do these therapeutic iron chelators and other compounds which have affinity for iron, affect the concentration of other metals? To attempt to answer this question, we have undertaken the present study. Complex formation between Al(III), Cd(II), Ca(II), Cu(II), Cr(III), Co(II), Mg(II), Mn(II), Ni(II) and Zn(II) with 3,4,5 trihydroxybenzoic acid was studied at different temperatures by a Potentiometric method. Potentiometric methods have been in use for some time for the determination of stability constant [6,6a].

In the present study computer program "BEST" was utilized for computation of stability constants from potentiometric data. The data file for this program requires the knowledge about

- i) total volume of the solution
- ii) molarity of the base used for pH titration
- iii) change in the pH after each step

- iv) number of millimoles of metal ions present in the solution
- v) number of millimoles of ligands present in the solution [7,8]. Finally the expected β values or the overall stability constants for each species present in the solution are given. The program calculates the sigma fit values [9]. The corresponding β value at minimum sigma fit is noted. The goodness of sigma fit reflects the accuracy of formation constant (K) values [9].

Thermodynamic stability of a species is a measure of the extent to which this species will form, or be transformed into, other species under certain conditions where the system has reached equilibrium [10].

A steady decrease in K values with increasing ligand concentration is expected due to slight changes in the metal ligand bond energies. The main reason for the change in bond energies of K values are, (1) Statistical factor (2) Increased steric hindrance (3) Coulombic forces in the complex. (4) Other coulombic forces involved in chelate ring formation.

The K values calculated at different temperatures are used to calculate ΔH and ΔS values [11,12].

As it is know that $\Delta G = -R \ln \beta$
 or $\Delta G = \Delta H - T \Delta S$
 Thus $\ln \beta = -\Delta H/RT + \Delta S/R$

As such a plot $\ln \beta$ vs $1/T$ will give $-\Delta H/R$ as slope and $\Delta S/R$ as intercept.

The Entropy effects can be discussed under the light of following factors. (1) Number of chelate rings. (2) Size of chelate rings (3) Arrangement of chelate rings. (4) Changes of solvation on complex formation. (5) Entropy variations in uncoordinated ligands (6) Effect resulting from differences in configurational entropies of the free ligands in the complex compound. The entropy values of different metal complexes were calculated and compared with literature values of Entropy of formation of complexes of these metal ions with other ligands [13,14].

Results and Discussion

The stability constant (K) values of the complexes at different temperature were used to calculate the thermodynamic values of complexes. ΔH and ΔS values for ML complexes of Mn, Ni, Cu, Al, Cr, Mg, Cd and Zn were calculated (Table-1, Fig. 1,2). It was found that transition elements having +2 oxidation state (Mn, Ni and Cu) have high enthalpy and entropy values. Whie +3 non transition elements like Al has comparable values with +2 transition elements like Zn(II) and Cd(II). Cr(III) was found to be an exceptional case in +3 transition elements.

Table-1: Formation constant of complexes ML.

Metal ions	Enthalpy KCal/mol.	Entropy Cal/mol.K
Mn	11.0	40.00
Ni	8.20	29.40
Cu	6.20	25.00
Al	1.80	15.00
Cr	2.50	13.40
Mg	2.10	12.80
Cd	1.90	8.60
Zn	1.00	10.00

When ΔH and ΔS ML_2 were studied (Table-2, Fig. 3,4), Co(III) was found to be a complex forming metal with very high enthalpy and entropy values. For the other metals there was no appreciable change in entropy or enthalpy values of ML_2 type of complex.

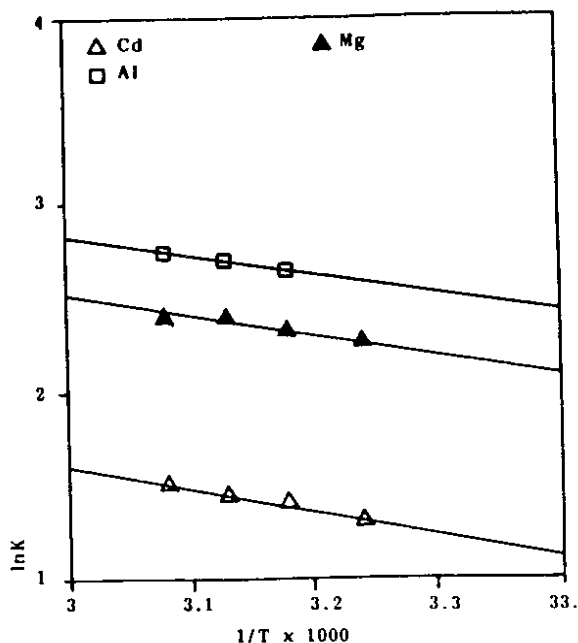


Fig. 1: Graph of the Heat Energies of M(GA). Where M = Al, Mg, Cd.

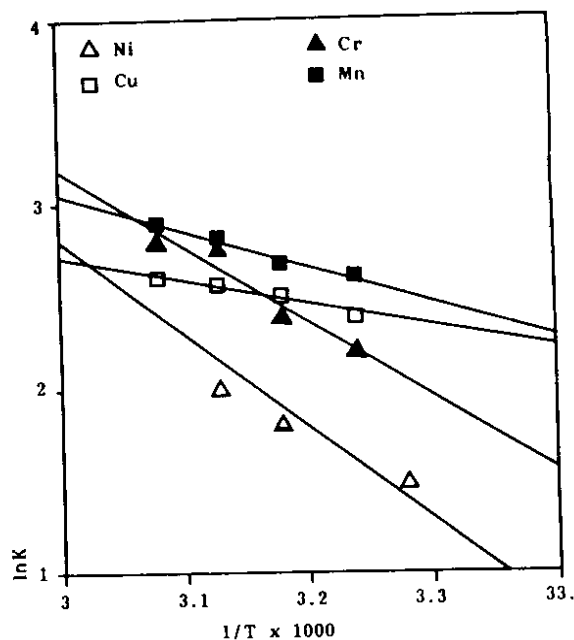


Fig. 2: Graph of the Heat Energies of M(GA). Where M = Mn, Cu, Ni, Cr.

For ML_3 complexes, it was found that only Co(III), Cr(III) and Mn(II) can form stable complexes having high ΔH and ΔS values. (Table-3, Fig. 5). When these values were compared with Iron Gallic acid complexes (Table-4), it was found

Table-2: Formation constant of ML_2 complexes.

Metal ions	Enthalpy value KCal/mol.	Entropy value Cal/mol.K
Co	11.0	38.6
Cd	4.80	19.50
Al	4.10	17.00
Mn	3.80	16.20
Mg	3.50	4.00
Cu	2.10	12.18
Cr	1.80	11.60
Ni	1.10	9.20
Zn	0.70	7.06

Table-3: Formation constant of complexes ML_3 .

Metal ions	Enthalpy value kCal/mol.	Entropy value Cal/mol.K
Co	8.0	28.00
Cr	1.40	11.00
Mn	0.50	7.20

Table-4: Enthalpy and Entropy values for iron gallic acid and iron gallic acid methyl ester complex.

	IRON GALLIC ACID COMPLEXES		IRON GALLIC METHYL ESTER	
	$\Delta H_{\text{cal}} \cdot K^{-1} \cdot M^{-1}$	$\Delta S_{\text{cal}} \cdot K^{-1} \cdot M^{-1}$	$\Delta H_{\text{cal}} \cdot K^{-1} \cdot M^{-1}$	$\Delta S_{\text{cal}} \cdot K^{-1} \cdot M^{-1}$
β_{111}	2.4	142	-	-
β_{110}	2.9	150	3.3	160
β_{210}	1.8	122	2.1	132
β_{310}	0.5	81	1.4	111

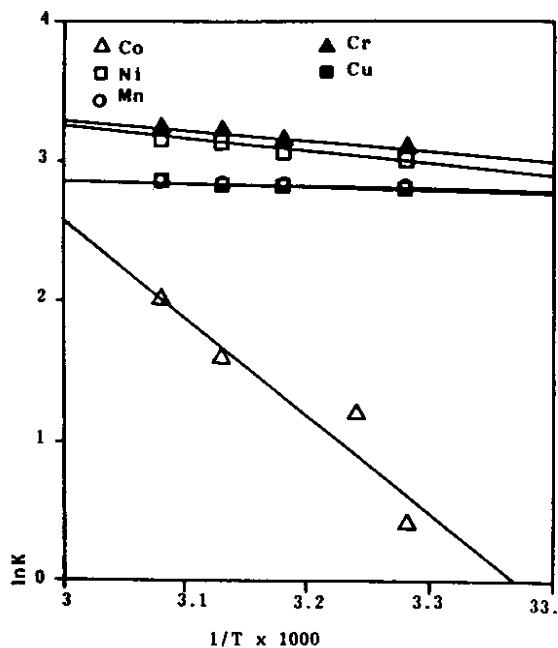


Fig. 3: Graph for the Heat Energies of $M(GA)_2$. Where $M=Co, Cr, Mn, Ni, Cu$.

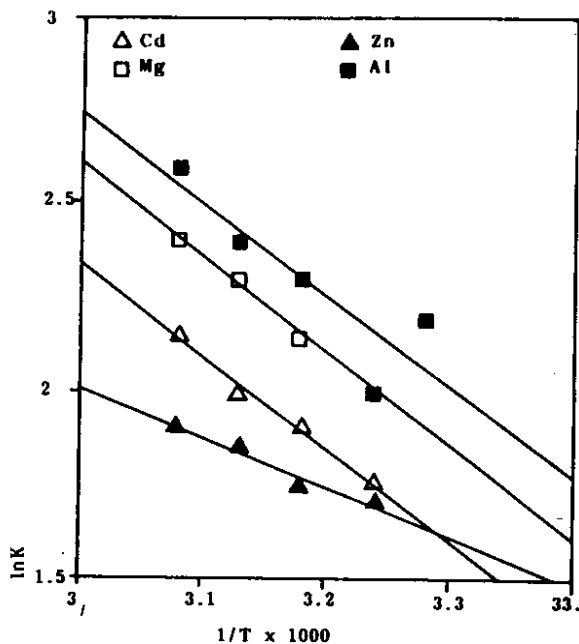


Fig. 4: Graph for the Heat Energies of $M(GA)_2$. Where $M = Zn, Mg, Cd, Al$.

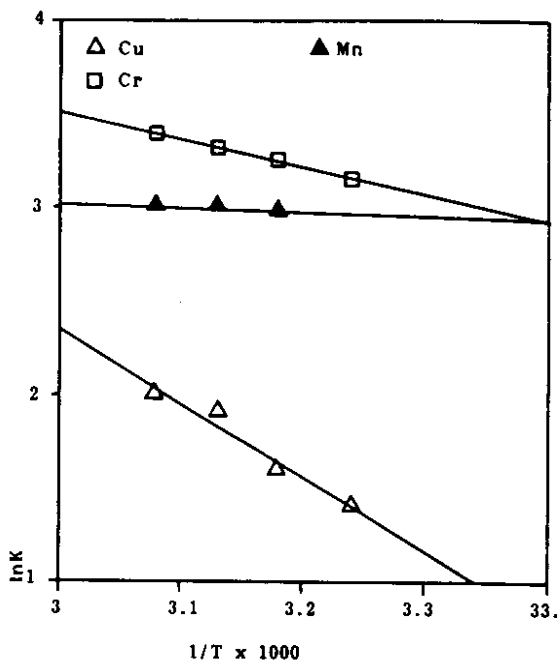


Fig. 5: Graph for the Heat Energies of $M(GA)_3$. Where $M = Co, Cr, Mn$.

that entropy values of Co, Ni and Cu are somewhat comparable with iron complexes while others have lower entropy values. However iron gallate has much higher ΔH and ΔS values. It is also found

that all metals show negative ΔG values except Ca(II) which has a negative ΔH .

Table-5: Enthalpy and Entropy values of different metal complexes.

Metal	Ligand	ΔH° Kcal.M ⁻¹	ΔS° cal.M ⁻¹	ΔH° Kcal.M ⁻¹	ΔS° cal.M ⁻¹
Mn ²⁺	malonic acid	3.7 ± .1	27.4	-	-
Zn ²⁺	***	3.0 ± .1	27 ± 4	-	-
Co ²⁺	succinic acid	3.2 ± 2	21	-	-
Cu ²⁺	***	4.5 ± 0.7	30.1	-	-
Mn ²⁺	***	3.0 ± 2	20.5	-	-
Ni ²⁺	***	2.5 ± 2	19.0	-	-
Zn ²⁺	***	4.4 ± .1	26.0	-	-
Co ²⁺	thiocarbazide	2.6	33.0	-	-
Mn ²⁺	1,1 diacetic acid	7.2	33.0	-	-
Zn ²⁺	***	3.1	37.0	-	-
Be ²⁺	salicylic acid	1.2	6.00	-	-
Co ²⁺	***	4.4	26.0	-	-
Cu ²⁺	***	3.7	9.00	-	-
Co ²⁺	thioisocyclic acid	7.3	52.0	5.00	40.0
Fe ²⁺	***	5.1	42.0	3.10	31.0
Mn ²⁺	***	4.1	38.0	5.70	37.0
Ni ²⁺	***	11.5	70.0	8.00	47.0
Zn ²⁺	***	6.50	60.0	9.10	58.0
Co ²⁺	phthalic acid	1.87	19.2	-	-
Mn ²⁺	***	2.20	19.9	-	-
Ni ²⁺	***	1.77	19.4	-	-
Zn ²⁺	***	3.20	23.8	-	-
Al ³⁺	CDTA	11.0	122	-	-
Mg ²⁺	***	1.60	52	-	-
Al ³⁺	DTPA	8.00	113	-	-
Mg ²⁺	***	3.00	52.4	-	-

Table-6: Enthalpy and Entropy values of iso-butyric acid with different metals

Metals	ΔH° Kcal.M ⁻¹	ΔS° cal.M ⁻¹	ΔH° Kcal.M ⁻¹	ΔS° cal.M ⁻¹
Ce ³⁺	3.33	18.6	2.6	13.6
Dy ³⁺	5.00	24.5	1.8	12.0
Er ³⁺	5.50	25.8	3.4	16.6
Eu ³⁺	2.90	18.8	1.9	12.2
Gd ³⁺	3.45	20.1	1.7	11.7
Ho ³⁺	5.30	25.3	2.6	14.1
La ³⁺	3.47	18.8	2.5	12.5
Lu ³⁺	5.40	25.5	3.7	17.4
Nd ³⁺	2.84	18.3	2.4	13.3
Pr ³⁺	3.04	18.4	2.5	13.5
Sm ³⁺	2.66	18.1	2.1	12.7
Tb ³⁺	4.40	22.6	1.5	11.3
Tm ³⁺	5.40	25.5	4.1	18.6
Y ³⁺	5.40	25.5	3.2	16.0
Yb ³⁺	5.40	25.4	4.0	18.1

When these values were compared with those of other complexes from literature (Table-5,6), following points were found to be noteworthy.

1. Monodentate ligands do not show any drastic entropy change with trivalent metals as compared to divalent metal.
2. Polydentate ligands show very high entropy values with tripositive metals.
3. Non transition metals show low entropy values with chelating agent.

It may be concluded that mutual coulombic repulsion between donor groups in metal chelate

are important, and the extent to which these repulsions are partially overcome in the free chelating ligand relative to analogous unidentate ligands is a manifestation of the enthalpy based chelate effect. Thus stability and specificity would be increased in all type of multidentate ligands by synthesizing structures in which the freedom of the donor groups to move away from each other is decreased as much possible. There are often geometric restrictions on the construction of compact multidentate chelating agents which prevent the most efficient utilization of donor group of atoms.

Experimental

Preparation of the solutions

All the solutions used for potentiometric titrations were prepared in doubly distilled, dionized and decarbonated water.

0.05 M solution of ferric nitrate was prepared by taking Fe(NO₃)₃ · 9H₂O from E. Merck. 0.05 M solution of others metals (all from E. Merck) was also prepared in the same manner. The salts of these metals taken were Aluminium Sulphate, Cadmium Chloride, Calcium Chloride, Copper Sulphate, Chromium Nitrate, Cobalt Chloride, Magnesium Sulphate, Manganese Sulphate, Nickel Sulphate and Zinc Sulphate. All the above metal solutions were standardized for their actual concentrations by standard methods.

Gallic Acid (3,4,5, trihydroxybenzoic acid) was obtained from E. Merck and was used without any further purification.

NaOH solution was standardized by standard HCl solution.

Potentiometric titration [15]

The titrations were carried out in a double walled glass cell fitted with an air tight stopper having three holes. These were used for nitrogen purging, for base addition and for the electrode to be dipped in the solution. The temperature of the cell was kept constant throughout the experiment with the accuracy of ±0.5° C by circulating thermostated water between the walls of titration vessel which could contain about 75 ml. solution.

pH were measured with a combination glass electrode attached to an ORION SA model 720 pH meter having a resolution of .001 pH unit. All the titrations were performed at 30°C, 35°C, 40°C, 45°C and 50°C.

For the titration 0.2 mmoles of gallic acid were mixed with 0.05 mmoles of metal ions in 50 ml solution and were titrated with 0.1M NaOH solution. The change in pH was noted with the small increment (0.05 ml) of base. Equilibrium condition, determined by a constant meter reading falling with in an interval of less than 0.002 pH unit, was obtained for each experimental point before proceeding with the next step. The solution was stirred with magnetic stirrer (IKAMAG E.C.T) constantly.

For each metal-gallic acid solution and each temperature these titration were performed twice to minimize the probable errors.

References

1. U. Miller-Eberhad, P.A. Miescher and E.R. Jaffe, "Iron Excess Aberrations of Iron and Porphyrin Metabolism" Grune and Stratton, New York (1977).
2. R.J. Walker and R. Williams, "Haemochromatosis and Iron over-load" in "Iron in Biochemistry and Medicine", A Jacobs and M. Worwood, Eds. Academic Press, New York (1977).
3. C.G. Pitt and A.E. Martell, "Chelating Agents" in "Inorganic Chemistry in Biology and Medicine" A.C.S. (1980).
4. A.E. Martell and R.M. Smith, "Critical Stability Constants" Vols. 1-4 Plenum, New York (1977).
5. H. Kipton, J. Powel and C.T. Michael, *Aust. J. Chem.*, **35**, (4), 739 (1982).
6. G.A. Carlson, J.P. McReynold and F.H. Verhock, *Aug. Acta Chem. Scan.*, **67**, 1334 (1945).
- 6a. F.J. Rossoti and H.S. Rossoti, *Acta. Chem. Scand.*, **9**, 166 (1955).
7. R.J. Motekatis and A.E. Martell, *Can. J. Chem.*, **60**, 2403, (1982).
8. R.J. Motekatis and A.E. Martell, *Can. J. Chem.*, **60**, 168 (1982).
9. A.E. Martell and R.J. Motekatis, *The Determination and Use of Stability Constant*, 2nd Ed. Publisher V.C.H. (1992).
10. S.J. Ashcraft and C.T. Mortimer, *Thermochemistry of Transition Metal Complexes* Acad. Press (1970).
11. R.T. Myers, *J. Chem. Educ.*, **53**, 17 (1976).
12. A.E. Martell, *Pure Appl. Chem.*, **50**, 813 (1978).
13. D. St. Black and A.J. Hartshorn, *Coord. Chem. Rev.*, **9**, 219 (1972).
14. F. Lysons, *Rev. Chem. Progr.*, **22**, 69 (1961).
15. Z. T. Maqsood, Ph.D. Thesis, Department of Chemistry, Unviersity of Karachi (1991).