

ANALYSING OF Eu (III) – PLANT AUXIN SYSTEMS THROUGH PH-METRIC TECHNIQUES

G.S. Chauhan*

ABSTRACT

Equilibrium analysis of Eu (III)- IBA/IPA/NAA system under thermodynamics conditions resulted in the composition of the system as 1:3 c metal-ligand; the resulting interaction surfaced as the chelation of metal with ligand with three primary and three secondary valencies. The successive lowering of stability of the systems in step-equilibria is ascribed the combined effect of statical, coulombic and steric factors. The stability and the thermodynamics of the systems involved are discussed. Varying opinions have been expressed on the mode of action of plant auxins, the controversy on this issue still hangs on Sawhney, Chauhan et.al. (1-4) studied some metal auxin system in solution and solid waste favouring chelation as a possible mode of action of plant auxins. This is an attempt on the analysing E(III) – Plant (IBA/IPA/NAA) systems under the thermodynamics conditions.

Keywords: *Eu(III), Coulombic, Steric Factors, COOH, Spectrophotometrically.*

Introduction

Few subjects in chemistry have excited more interest and more resultant controversy than the subjects of metal complexes, which have the wide spectrum of applications beginning with analytical chemistry and ending with medicinal chemistry. Botanists are faced with the nature of interaction of plant auxins with metal ions present in soil : they have been baffled for a long time. The first comment on the subject came from Koepfli, Thimann and Went (5). The Conclusions based upon the investigation on the number of compounds had a tally with presence of a ring system with at least one double bond with least one carbon atom between the ring and –COOH group in an active growth substance. The subsequent results collected by Heath and Clark (6) were to the contrary. Without recourse to experimentation, they suspected the plant auxins to act as Chelating agents. Cohen and coworkers (7), could provide to some extent the clues for chelation as possible mode of action for plant auxins, using stability data on Cu (II) – IAA and Cu (II) –NAA as an aid in jumping on such conclusions. Recaldin and Heath (8) later on ascertained the preceding inferences. Light on the involvement of two functional groups in chelation as shown below, was thrown by Van Overbeek (9).

In the light of controversy still hanging on the subject mode of action of plant auxins, it has been felt to pursue and continue studies on metal-plant auxin interaction in solution and solid state. The systems, on which the decision to build on was taken, are

- Metal – IBA
- Metal – IPA
- Metal – NAA

where the metals which form the part of the systems are: Eu (III), Gd (III), Tb (III) and Dy (III)

Early Activity on the Subject and Its Allied Areas

Daijiro (10) investigated spectrophotometrically the activity of IAA to complex Fe(III) in solution.

Highlight of the work of Oata and Coworkers (11) are the action patterns of 3-indole acetic acid and gibberelic acid on the growth of duckweed, similar to those reported for agents that chelate both Cu (II) and Fe (II)/Fe (III).

* Department of Chemistry, D.A.V. (P.G.) College, Dehradun, Uttarakhand, India.

Solanki and his associates (12, 13) worked on the compositional and conformational aspects of the metal complexes of IAA and of IBA with La(III), Pr(III), Nd(III), Th (IV), Whereas Sahai (14) could demonstrate the affinity of Mg(II), Co(II), Ni(II), Cu(II), Al(III), Fe(III), La(III) and Th(IV) pH-metrically, Conformational studies on lanthanides complexes were made by Levine (15). In 1973 Kovacs Erzsébet's (16) reported on the formation of auxin macromolecular complexes in plant organs of various ages.

Chakraborty and his associates (17) reported indole compounds by circular chromatography while two dimensional chromatography was depended upon by Paul Emile (18). Solon (19) estimated quantitatively IAA in plant preparations chromatographically. Holbrokke and coworkers (20) saw plasma insulin activity in human diabetes during hypoglycemic response to tolbutamide and indole-3-acetic acid.

Klammt (21) could detect IAA (indole-3-acetic acid)

The subject matter, this thesis embodies, is concerned with the solution and solid state chemistry of the interaction of some of the plant auxins : indole-3-butyric acid (IBA), indole-3-propionic acid (IPA) and 1-naphthalene acetic acid (NAA), and some of the lanthanide series elements : Eu(III) etc.

Line of action followed has to be briefed.

Feasibility of Eu-IBA, Dy-NAA, Eu-NAA, Dy-IPA reaction, as evidenced by the more negative ΔG values at higher temperature (350C) increased. The observed ΔH values for all the reaction suggested these reactions as endothermic in nature, and signalled further the presence of covalency in metal-point auxin complexes. All the reactions are accompanied by an increase of entropy ($+\Delta S$) and tend to be spontaneous. Relieved Perrot-Rechenmann(22), Plant Auxin, regulates many critical aspects of plant growth and development by directing cell division.

Lc Strader, Bortel(23), Transport and metabolism of the Endogenous Auxin precursor indole-3-butyric acid.

Gangwar et al(24), Physiology and biochemistry of plants.

Vanhoutel et al, Thounosian et al(25) Besides the direct impact of heavy metals on plants, they can also cause cytotoxicity by overproduction of reactive oxygen species (ROS), which impairs antioxidant defence system and causes oxidative stress.

LBuceke Ne to(26), Interaction between plant hormones and heavy metals.

Bennett, T. Pin (27), proteins and the evolution of plant development.

Kasahara, H. (28), Current aspects of auxin biosynthesis in plants.

Experiments

The chemicals used were of analytical grade [A.G.]. The instrument and, reagents used are as :

KHNO₃ : 0.1 M (aq)
 KNO₃ : M (aq)
 NaOH : 0.1 M (aq)
 Ligand : IB/IPA/NAA

Result and Discussion

Within a thermodynamically true environment attainable at infinite dilution and constant ionic strength (0.02 MKNO₃), the pH titration was performed IBA, IPA AND NAA contain a titratable H⁺ as a consequence of ionisations of carboxylic group C- (OO), making the study of these systems possible. The protonation constant of IBA, IPA, NAA (Table 1) could be worked out by applying the concept of Henderson and Rosotti (29).

Protonation constant ($^pK^H$)

Medium : 50% aqueous dioxin

Ionic Strength : 0.02 M KNO₃

Table 1: Protonation constants at IBA, IPA, NAA

Auxin	Log $^pK^H$	
	25 ^o C	35 ^o C
IBA	5.60	5.10
IPA	5.45	4.80
NAA	5.60	4.70

The whole study was performed under conditions of infinite dilution and constant ionic strength, at which only mononuclear species are formed, and so could meet the basic condition at the Bjerrum Technique (30). In homogeneity was not observed in 50% D/W solvent (50% dioxine (D) in water (w)). Through the pH titration at $25 \pm 1^\circ\text{C}$ and $35 \pm 1^\circ\text{C}$ (Fig. 1a&1b, 2a&2b & 3a&3b).

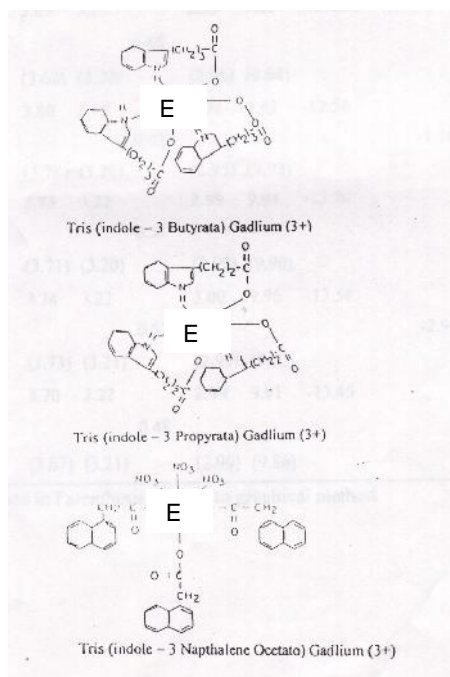
$$PL = \frac{1 + 10^{(PKH - pH)}}{NaOH}$$

Bjerrum's equation which can be scope sented in simplified form as was employed as an aid in working out the legand number (n) and free legand exponent (PL) as free legand exponent (PL) values corresponding to various pH values. The free legand (PL) free legand exponent together with the legand number (n) values (extent of complexation) had been useful in determining the stability constants, then at the systems. Eu-IBA, Eu-IPA and Eu-NAA was close to 3 demonstrating the presence of 1:1, 1:2, 1:3 species in solution from fermation curves of the systems (n versus PL), the ratio of stepwise formation constants, i.e. $\log K_1/K_2$ fell below the value 2.5, which is basic to the applicability which is of the method in the estimation of metal ligand formation constants, the graphical method was adopted according to the using equation.

$$\text{Log Kn} = pL + \log \frac{[n - (n - 1)]}{(n - n)}$$

The stability data given in Table 2 which showed the following order for log kn values, $\log K_1$, $\log K_2$, $\log K_3$ decrease with increasing temperature following a low temperature for complex formation, this appear to be due to decrease in the number of collosions with kinetic energy of the molecule invalued in the reaction . But in Eu-NAA system the value of $\log K_1$, $\log K_2$ and $\log K_3$ increases with increasing temperature, which indicate the higher temperature favour the complex formation. The reaction between Eu-IPA, Eu-IPA and E-NAA systems are spontaneous as indicated by the negative ΔG value, the feasibility of the reaction increased as evinced by the increased negativity ΔG at higher temperature. The observed ΔG values for all the reaction suggested these reactions as endothermic in nature and signalled further the presence of covalency in metal-plant auxin complexes. All the reactions are accompanied by an increases of entropy ($+\Delta S$) and tend to be spontaneous.

As the result of the present study, the accompanying structures appears to be the only possibilities represented in Scheme I.



Scheme 1

Table 1a: The stability constants and Thermodynamics parameters of the different Metal-Plant Auxin Systems

System	Temp. °C	log					UG	UH	US
		K ₁	K ₂	K ₁ /K ₂	K ₃	S ₃			
Eu (III) – IBA	25	3.79	3.21		2.99	9.99	-13.44		
				0.58					
		(3.67)	(3.20)		(2.98)	(9.95)		-1.68	
	35	3.69	3.21		2.98	9.87	-13.49		+38.34
Eu (III) – IPA	25	3.76	3.20		3.00	9.96	-13.55		
				0.56					
		(3.75)	(3.20)		(2.99)	(9.94)		-2.52	
	35	3.70	3.21		2.98	9.89	-13.47		+35.55
Eu (III) – NAA	25	3.68	3.21		2.99	9.88	-13.43		
				0.47					
		(3.66)	(3.20)		(2.99)	(9.85)		-2.20	
	35	3.70	3.22		3.00	9.92	-13.50		+36.68
			0.48						
		(3.70)	(3.20)		(3.00)	(9.90)			

Values in parentheses are due to graphical method.

ΔG and ΔH in Kcal. mol⁻¹ ΔS is cal mol⁻¹ °C⁻¹.

The exothermic nature of those reactions could be based upon the negative H values, which signaled the existence of covalency in Eu-plant auxin complexes. The Eu-IBA – IPA, - NAA reactions are accompanied by an increase of entropy (positive ΔS) and tend to spontaneous (See Table 2).

This study indicates that the structure shown in Scheme 1 appear to be the only possibilities.

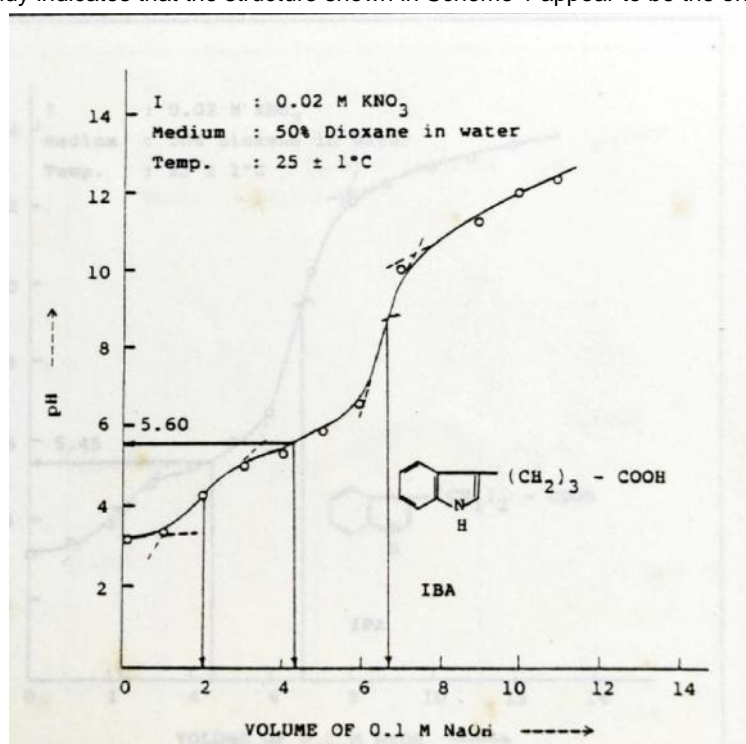


Fig. 1a : pH-Metric Titration of IBA+HNO₃ with NaOH

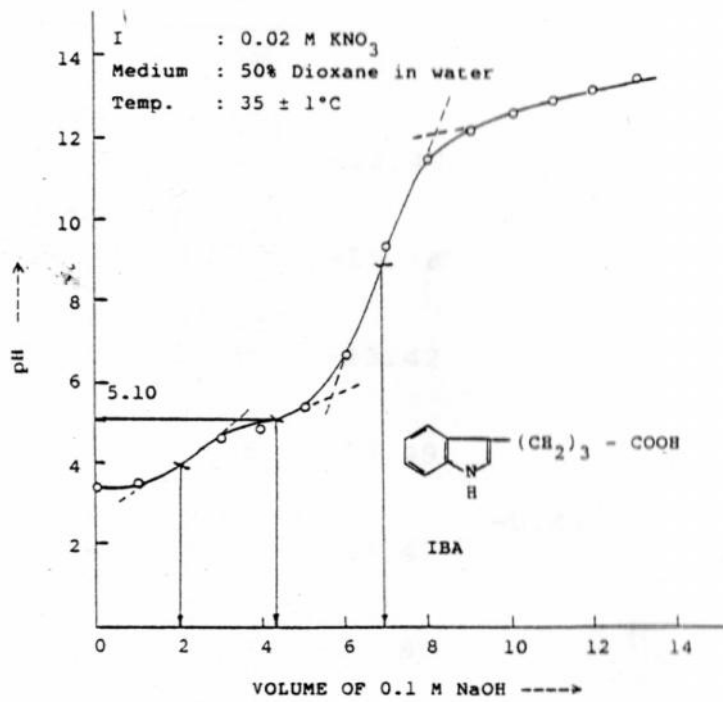


Fig. 1b : pH-Metric Titration of IBA+HNO₃ with NaOH

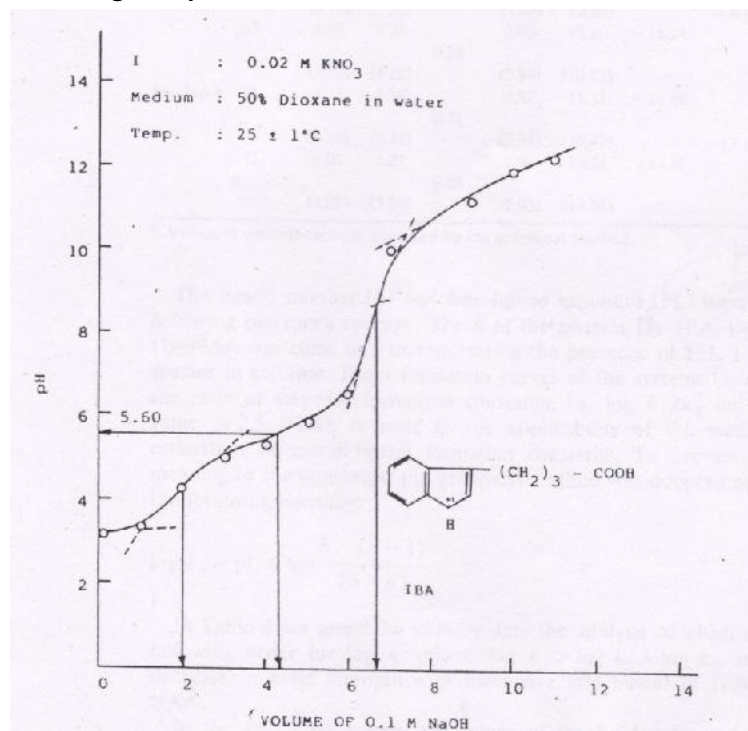
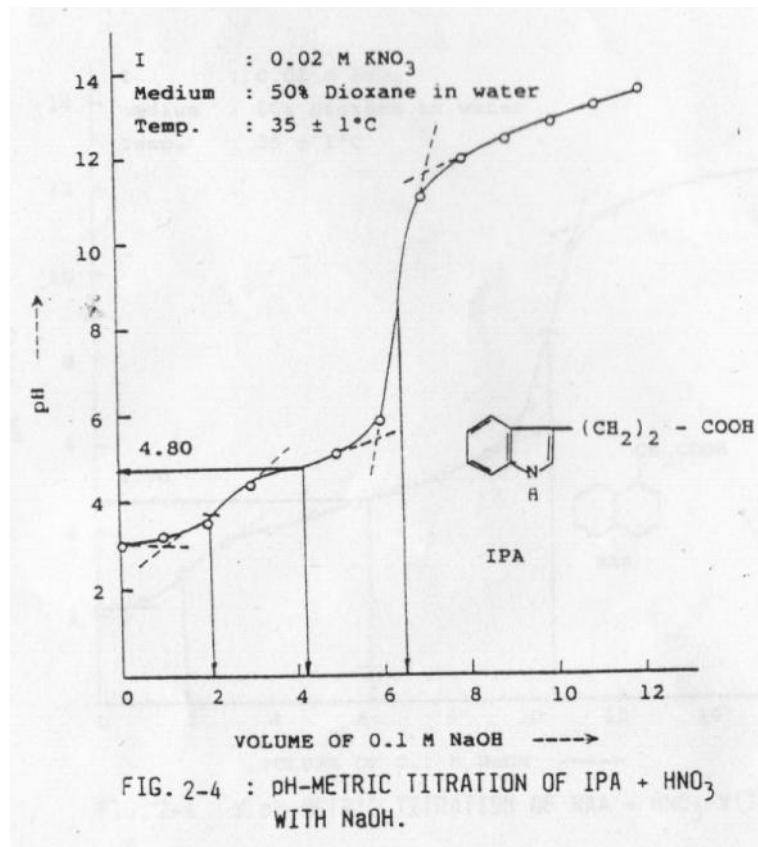
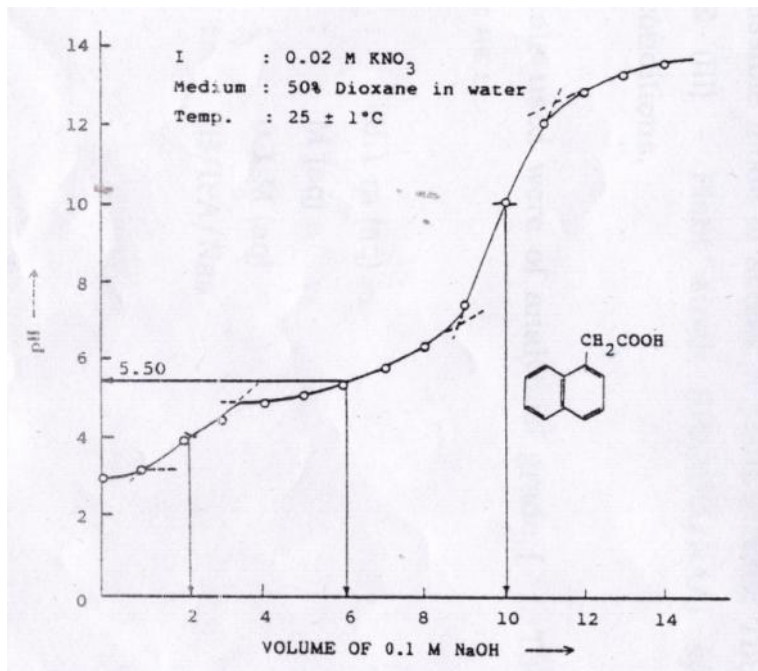


Fig. 2a : pH-Metric Titration of IPA+HNO₃ with NaOH

Fig. 2b : pH-Metric Titration of IPA+ HNO_3 with NaOHFig. 3a : pH-Metric Titration of NAA+ HNO_3 with NaOH

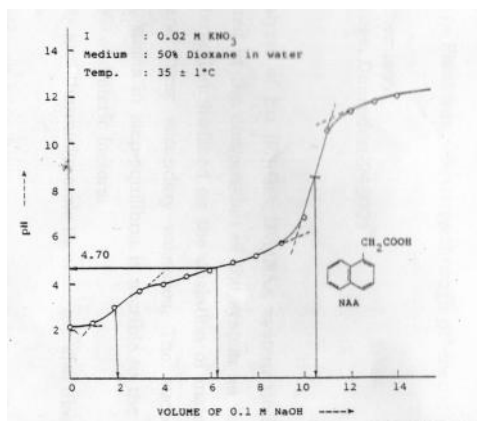


Fig. 3b : pH-Metric Titration of NAA+HNO₃ with NaOH

References

- ✠ B. Levine, M. J. Thornton and J.P.R. Williams J. Chem. Soc. Chem. Commun., 16 (1974) 70.
- ✠ Bennett, T. pin proteins and the evolution of plant development. Trends Plant Sci. 2015,20,498-507..
- ✠ D. Cohen, B. L. Ginzburg and C. Heitner Werguin, Nature, 181 (1958) 686.
- ✠ D.A. Recaldin and O.V.S. Heath, Nature, 182 (1958) 539.
- ✠ G. A. Solon and P.G. Lasli, U.S. Atomic Energy Comm. ANL. 47-50 (1956) 5597.
- ✠ Gangwar et al, zhang et al (2010), (2011).
- ✠ H. C. Chakroborty and S. P. Sen, Naturuissens Chapter 42, (55) 512.
- ✠ H. Irving and H. Rossotti, J. Chem. Soc., (1953), 3397; (1954), 2904
- ✠ H.D. Klambt, Ber. Deut. Ges., 72 (1959) 185.
- ✠ J. B. Koepfli, K. V. Thimann and F.W. Went, J. Biol. Chem., 122(1938) 763.
- ✠ J. Bjerrum, Metal Ammine Formation in Aqueous Solution. p. Hasse and Son, Copenhagen, 194,P.298.
- ✠ J. Van Overbeek, J. Bot. Rev. 25(1959) 6269.
- ✠ K. Solanki and A. M. Bhandari, J. Inorg. Nucl. Chem. 41(9) (1976).
- ✠ K. Solanki, K. R. Mehar and A. M. Bhandari, Synth. React. Inorg. Met. Org. Chem., 8(4) (1978) 335.
- ✠ Kasahara, H. Current aspects of auxin biosynthesis in plants. Biosci. Biotechnol. Biochem. 2016,80,34-42
- ✠ Koves Erzsebet and Ilona Kovacs, Acta Biol. Szedged., 18(1-4) (1972) 117.
- ✠ Lc Buceker Ne to(2017).
- ✠ Lc Strader, B Bortel, (2010).
- ✠ O.V.S. Heath and J. E. Clark, Nature, 197(1957), 1118, 178(1956) 600; 183 (1959) 1177.
- ✠ Pual Emile, Pilet Compt. rend., 247 (1958) 605.
- ✠ R. Sahai, S.S.S. Kushwaha and A. K. Chaudhary, J. Indian Chem. Soc. 57(8) (1980) 844.
- ✠ Relieved perrot-Rechnmann, (2010)
- ✠ S. S. Holbrooke and L. S. Wolter, Proc. Soc. Exptl. Biol. Med., 100 (1959), 171.
- ✠ S.S Sawhney, N. C. Sharma and N.K. Arora, Thermochem. Acta, 126 (1988) 393-395.
- ✠ S.S. Sawhney and N.C. Chandra, Thermochem. Acta, 115(1987) 375-380.
- ✠ S.S. Sawhney and R.K. Mittal,Thermochem. Acta, 138 (1989) 173-175.
- ✠ S.S. Sawhney, Gambhir Singh Chauhan and Naresh Chandra, Thermochem. Acta, 144 (1989) 173-175.
- ✠ Vanhoutol et al, Thounosian et al. (2016)
- ✠ Y. Daijiro and I. Naomichi, Meiji Daigaku Nogakuku Kenkum Hokoku, 9 (1959) 19.
- ✠ Yokito Oata, Takaliko Tsudzulki, Plant Cell Physiol, 12 (4) (1971).

