

EQUILIBRIUM ANALYSIS AND THERMODYNAMIC STABILITY PARAMETERS OF Gd (III)- PLANT AUXIN SYSTEMS

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ABSTRACT

In spite of advances, critiques and counters critiques on the mode of action of plant auxins, the controversy on this issue still hangs on. Sawhney, Chauhan et.al. (1-8), contributed greatly knowledge at the metal affinity to plant auxin in solution and solid state. The subject matter, this paper 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- nappthalene acetic acid(NAA), and some of the lanthanide series elements:M(III), etc. have been taken as model studies under thermodynamic conditions.. This is an attempt to carry out an equilibrium analysis of Gd(III) -IBA, Gd(III) - IPA and Gd(III) -NAA systems at constant ionic strength and at infinite dilution, to give an explanation of the stability and thermodynamics of these systems.

Keywords: Gd(III), Critiques, Controversy, Auxin, Thermodynamics, Collusion, Carboxylic Group.

Introduction

Some subject in interdisciplinary research have excited more interest and more resultant controversy than the mode of action of plant auxins; this area has baffled and continues to puzzle the Botanists. Different opinions have been expressed on the mode of action of plant auxins. This is an extension, of the line of action Claiming chelation as a possible mode of action for plant auxins. The importance and necessity of taking up of this subject: metal-plant auxins interaction. The first comment on the subject matter came from Koepfli, Thimann (9).The conclusions based upon the investigation on the number of compounds had a tall with the presence of a ring system with at least one double bond with a side chain carrying a carboxyl group, and there being at least one carbon atom between the ring and Carboxylic (-COOH) group in an active growth substance. The subsequent results collected by Heath and Clark(10),were to the contrary. Without recourse to experimentation, they suspected the plant auxins to act as chelating agents. Cohen and coworkers (11),could provide to some extent the clues for chelation as possible mode of action for plant auxins, using stability data on Cu(II) -IPA and Cu(II) -NAA as an aid in jumping on such conclusions. Recaldin and Heath(12),later on ascertained the preceding inferences. Light on the involvement of two functional groups in chelation, was thrown by Van Overbeek. (13) 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.

Highlight on the Early Activity of the Subject and its Allied Areas

Highlight of the work of Oata and coworkers (14) are the action patterns of 3- indole acetic acid, similar to those reported for agents that chelate both Cu(II) and Fe(II) /Fe(III).

Solanki and his associates (15,16),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 (17),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(18).

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Klambt (19), could detect IAA(indole- 3- acetic acid) chromatographically while Mendez(20),carried out spectral studies on IAA.

The effect of organic copper complexes on the glutathione status of fed rats has been seen by Harisch and his associates (21), highlighting the rise or fall of GSH level in liver with the rise and fall of the complex dose.

Sawhney and his associates (22-25),worked on the affinity of some of the plant auxins:IAA, IBA, IPA and NAA to metal ions:Ce(III), Pr(III), Nd(III) Pm(III), Sm(III) in solution as well as in solid state, highlighting their stoichiometries, stability and thermodynamics.

Korshak and associates (26),explained the mechanism of the reaction of polyglycidyl methacrylate with carboxylic acids(-IBA, IPA), phenylacetic acid, 2,4-dichlorophenoxy acetic acid.

Analytical investigation of some flurogenic reaction of indole- 3- lactic acid with o-phthalaldehyde was done by Terezo and his colleagues (27),thin layer chromatographically.

Hussein and associates (28),reported on the effect of some alcohols and plant auxins on the biosynthesis of oleandomycin, and role of precursors in oleandomycin biosynthesis by streptomycetes antibiotics.

Liux, Barkawil, Gardner G, Cohen JD. (29), Trnsport of indole-- 3- butyric acid and indole- 3- acetic acid in arabidopsis hypocotyls using stable isotope, labeling. plant physiology.

Cruz H, Lopez-Bucio J, (30), Auxins differentially regulate root system architecture and cell cycle protein levels in maize seedlings.

Starder Lc, Bartel B. (31), The arabidopsis pleiotropic drug resistance 8/ABCG36ATP binding cassette transporter modulate sensitivity to the auxin precursor indole- 3 -butyric acid.

Strader Lc, Culler AH, Cohen JD, Bartel B. (32),conversion of endogenous indole- 3-buthric acid to indole- 3-acetic acid drive cell. expansion in arabidopsis seedling.

R. Abualia, E. Benkova, B. Lacombe (33), Transporters and mechanism of hormone transport in Arabidopsis, Adv. Bot. Res;87, 115-138(2018) pp.

H. R. Allen, M. Ptashnyk(34), Mathematical modelling of auxin transport in plant tissues;flux meets signalling and growth. Bull. Math. Biol. 82,35(2020)pp

Experimental

The chemicals used were of analytical grade. The instrumental and experimental conditions also described, and kept here.

Reagents

- Nitric acid: 0.1 M (aq)
- Potassium nitrate:M(aq)
- Sodium hydroxide: 0.1M(aq)
- Ligands: IBA/IPA/NAA
- Solvent :Dioxane
(Metal Salt: Gadolinium nitrate (aq))

Apparatus: Digital pH- Meter Eleco,

Model Li-120 etc.

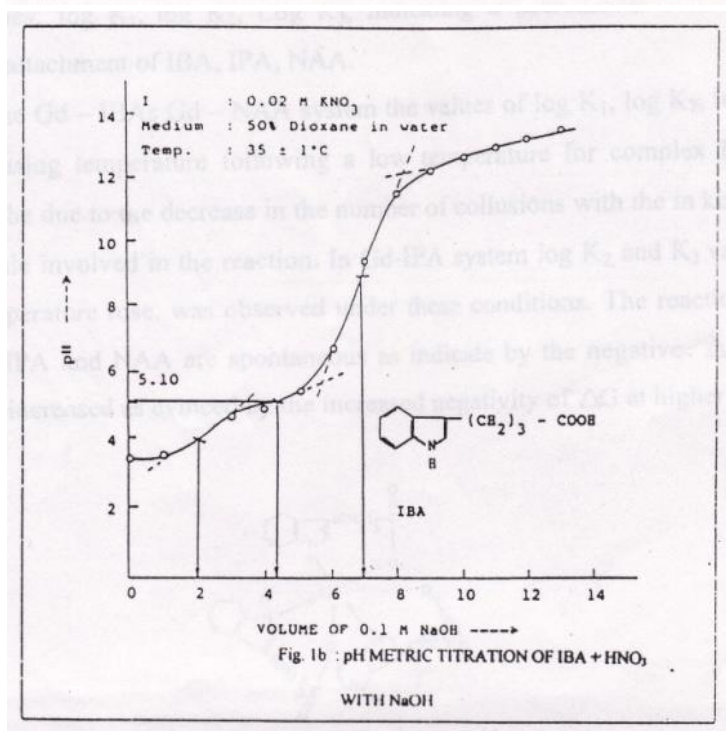
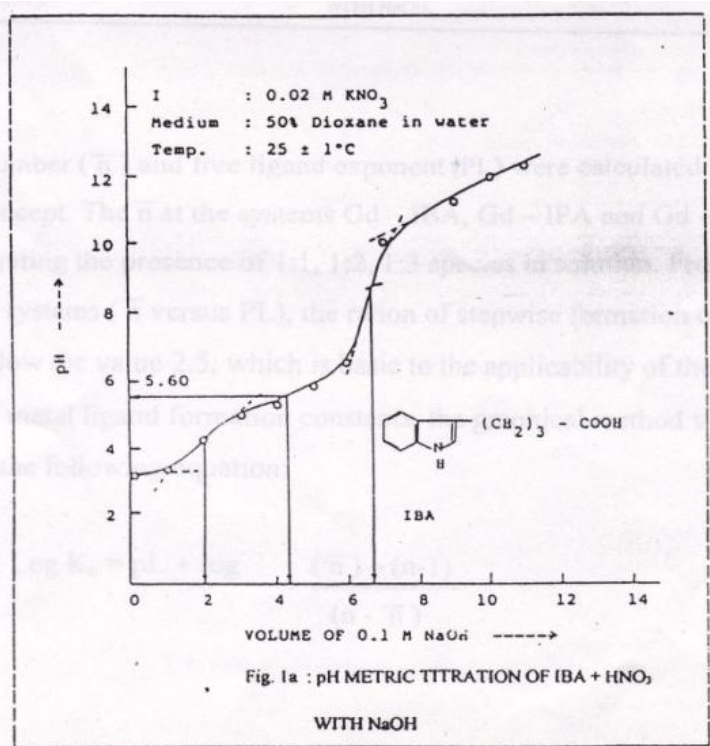
Results and Discussion

Within a thermodynamics true environment attainable at infinite dilution and constant ionic strength, (0.02 MKNO₃) the pH-titration was performed. IBA, IPA and NAA contains a titrable H⁺ as a consequence of ionisation of carboxylic group, making the study of these systems possible. The protonation constant of IBA, IPA, NAA (Table 1) could be worked out applying the concepts of Henderson and Irving and Rossotti (35).

Table 1 : Protonation constants AT IBA, IPA, NAA

Auxin	Log ^P K ^H	
	25 ⁰ C	35 ⁰ C
IBA	5.60	5.10
IPA	6.45	4.80
NAA	5.60	4.70

All worked was carried out at infinite dilution, at which only mononuclear species are formed and so could meet the basic conditions at the Bejerrum technique (36),In homogeneity was not observed in 50% D/W solvent (50% dioxane (D)) in water (W) through the pH (titration) (Fig. 1a + 1b).



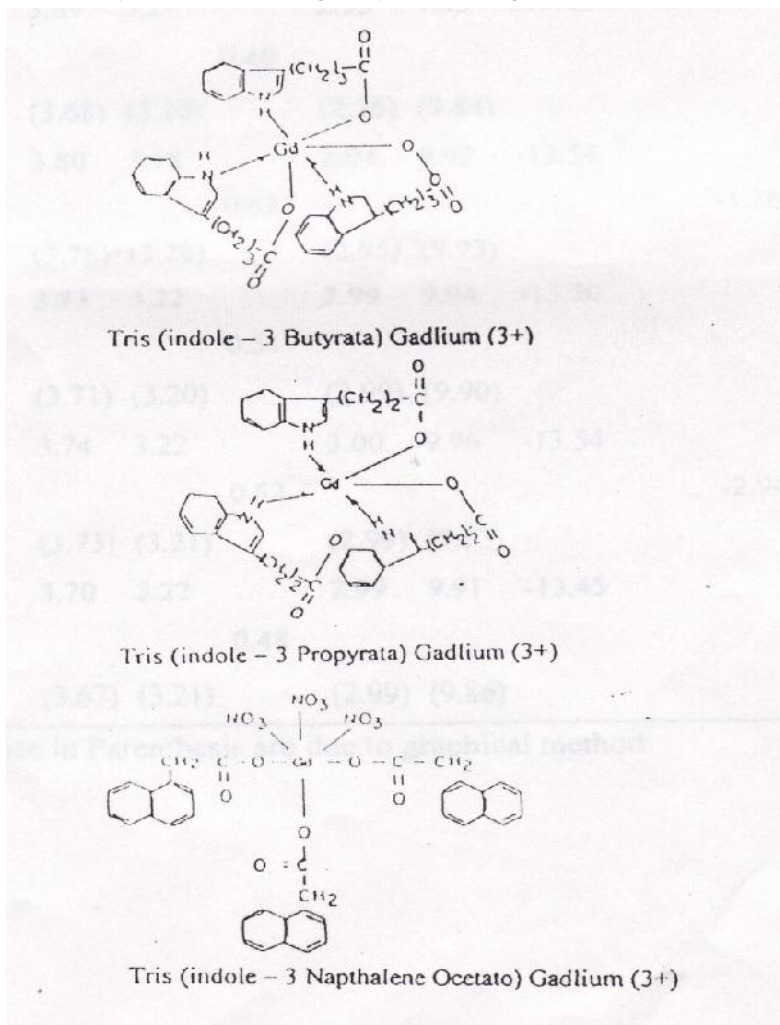
The ligand number (n) and free ligand exponent (PL) were calculated following Bjerrum's concept. The n at systems Gd – IBA, Gd – IPA and Gd – NAA was close to 3 demonstrating the presence of 1:1, 1:2, 1:3 species in solution. From formation curves of the systems (n versus PL), the ratio of stepwise formation constants. i.e. $\log K_1/K_2$ fell below the value 2.5, which is basic to the applicability of the method in the estimation of metal ligand formation constants, the graphical method was adopted according to the following equation:

$$\log K_n = pL + \log$$

$$\frac{(\bar{n}) - (\bar{n} - 1)}{(n - n)}$$

In table 2 are given the stability data the analysis of which showed the following order for $\log K$ values: $\log K_1$, $\log K_2$, $\log K_3$, indicating a decrease in bond strength with successive attachment of IBA, IPA, NAA.

In the Gd -IBA, Gd- NAA system the values of $\log K_1$, $\log K_2$, $\log K_3$ decrease with increasing temperature following a low temperature for complex formation; this appears to be due to the decrease in the number of collisions with the in kinetic energy of the molecule involved in the reaction. In Gd-IPA system $\log K_2$ and K_3 values increase as the temperature rose, was observed under these conditions. The reaction between Gd and IBA, IPA and NAA are spontaneous as indicate by the negative ΔG value, their feasibility increased by the increased negativity of ΔG at higher temperature.



Scheme 1

Table 2: The stability constants and thermodynamics Parameters of the Gd (III) – IBA, Gd (III) – IPA and Gd (III) – NAA systems.

System Temperature (°C)		log				B ₃	UG (Kcal/mol)	UH (Kcal/mol)	US (cal/mol) °C ⁻¹
		k ₁	k ₂	k ₁ /k ₂	k ₃				
Gd (III) IBA	25	3.84	3.24		3.01	10.09	-13.73		
				0.60					
		(3.82)	(3.23)		(3.00)	(10.05)		-8.82	
	35	3.69	3.21		2.95	9.85	-13.42		+14.49
				0.40					
		(3.68)	(3.20)		(2.96)	(9.84)			
Gd (III) IPA	25	3.80	3.18		2.94	9.92	-13.54		
				0.63				-1.26	
		(3.78)	(3.20)		(2.95)	(9.93)			+39.74
	35	3.73	3.22		2.9	9.94	-13.50		
				0.51					
		(3.71)	(3.20)		(2.99)	(9.90)			
Gd (III) NAA	25	3.74	3.22		3.00	9.96	-13.54		
				0.52				-2.94	
		(3.73)	(3.21)		(2.99)	(9.93)			+34.12
	35	3.70	3.22		2.99	9.91	-13.45		
				0.48					
		(3.67)	(3.21)		(2.99)	(9.86)			

Values in parenthesis are due to graphical method.

The exothermic nature of those reactions could be based upon the negative H values, which signaled the existence of covalency in Gd-plant auxin complexes. The Gd-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.

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