Equilibrium Analysis of IAA, IPA and IBA with Metals

Man Mohan Singh Jassal
Department of Chemistry
D.A.V. (P.G.) College, Dehradun, Uttarakhand

Abstract
This paper reports on the affinity of metals Nd (III) and Y(III) to plant auxin. Indole-3-acetic acid (IAA), Indole-3-propionic acid (IPA) and Indole-3-butyric acid (IBA) at constant ionic strength (0.1M KNO$_3$) and infinite dilutions. Research has been initiated to resolve the puzzle and to arrive at some conclusion. These conditions help to maintain thermodynamic environment essentially required to equalize the values of conditional formation constant and thermodynamic formation constant. The stability and thermodynamics of the systems involved are discussed.

I. Introduction

The views of researchers investigating plant auxin activity are at variance. Some have concluded that chelation is a possible mode of action of plant auxins[1-5]. The positional status of the carboxyclic and –NH groups on the surfaces of IAA, IPA, IBA molecules sign both the possibilities of salt formation and complexation when these molecules are brought in contact with the metal ion(s) in solution under optimal conditions or thermodynamic conditions. In order to settle on the either of the above possibilities, and the mode of the action of these plant auxins in reference, the solution study has been done on the equilibrium analysis of the system(s) containing a metal ion and either of plant auxins in non-aqueous medium at infinite dilution and at constant ionic strength.

II. Experimental

All the ligands and metal salts used were of analytical grade. Plant auxins solution were prepared in 50% 1, 4- dioxane/distilled water and metal nitrate solutions were prepared in cation free distilled water. For solution studies, solutions having identical concentrations of the common ingredients in different sets were prepared, according to Bjerrum and Calvin[6]. The pH was corrected for non-aqueous media (50% v/v 1,4 – dioxane/distilled water) as recommended by Van Uitert and Hass [7] and was measured on a Toshniwal pH-meter model Cl-54 with sensitivity of ±0.5 was duly standardised with the suitable buffers. The ionic strength was maintained at 0.1M KNO$_3$. Three sets were prepared as termed in (A), (B) and (C) and pH metrically titrated against 0.1M NaOH at two temperature (25^0 and 35^0C).

(A) 2×10^{-3} M HNO$_3$ + 1×10^{-1}M KNO$_3$

(B) 2×10^{-3} M HNO$_3$ + 20×10^{-4}M plant auxin (ligand) + 1×10^{-1}M KNO$_3$

(C) 2×10^{-3} M HNO$_3$ + 20×10^{-4}M Plant auxin + 2×10^{-4} M metal ion + 1×10^{-1} M KNO$_3$

III. Results and Discussion

All plant auxins are monoprotic. Equilibrium analysis of metal plant auxins systems under thermodynamic conditions achieved adhering to infinite dilution and constant ionic strength could be realised, pH metrically with the calculation of the different factors such as $^PK^H$, pL, Kn, n̄, ΔG, ΔH and ΔS, utilizing the resulting pH Vs NaOH Curves

The pH titration of the binary mixture of acids [(HNO$_3$) and mono protic acid (plant axuin)] resulted in two inflexions representing HNO$_3$ (first inflexion) and plant auxin (second inflexion) confirming the titrable hydrogen as one only in each of plant auxins : IAA, IPA and IBA. The examination of the pH curves showed the separation of metal lignand curve from ligand curve indicating the release of protons in solution due to metal ligand interaction, resulting in the complexation or chelation depending the positional status of groups involved in the interaction of IAA, IPA and IBA, which has a potential to form metal complexes.

The Interaction was gradual with the gradual increase of n̄ value which ultimately assumed limiting value. The n̄ value was found to be nearly 3 suggesting that three types of complexes or chelates were formed 1:1, 1:2, 1:3 under experimental condition. The protonation constants of IAA, IPA and IBA could be workout by applying the concept of Henderson [8], Irving and Rossotti[9]. The refined values of the protonation constants of metal-plant auxin sysem are compiled in Table 1 at 25^0±1 and 35^0±1.

Table 1
Protonation Constant of Plant Auxins

S.No.	Plant Auxin	log $^Pk^H$	
		25^0 C	35^0 C
1	Indole-3-acetic acid (IAA)	6.40	6.10
2	Indole-3-propionic acid (IPA)	6.60	6.30
3	Indole-3-butyric acid (IBA)	7.10	6.80

The IAA, IPA, IBA are bidentate complexing agents armed with potential to replace two monodentate complexing agent like H_2O. The metal salts when dissolved in H_2O forms aquometal complexes depending upon the ligand of the metal i.e. $M(H_2O)_n$ were n is metal ligancy

$$M(H_2O)_n + PAH \xrightarrow{K_1} M(H_2O)_{n-2}.PA + H^+$$

$$M(H_2O)_{n-2}.PA + PAH \xrightarrow{K_2} M(H_2O)_{n-4}.(PA)_2 + H^+$$

$$M(H_2O)_{n-4}(PA)_2 + PAH \xrightarrow{K_3} M(H_2O)_{n-6}.(PA)_3 + H^+$$
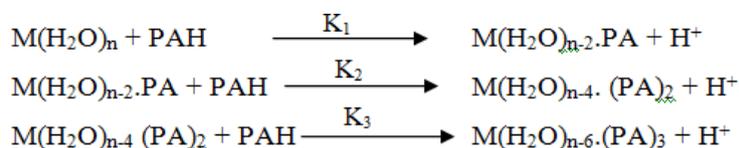
where, PAH = plant auxin shown with the ionisable hydrogen H from COOH group and K_1, K_2, K_3 are the stepwise formation constants.

The metal-auxin stability constant were evaluated fowlloign Bjerrum's concept[6]. The systems as shown by formation curve ($\bar{n}$ vs pL) could not acquire the condition necessary for Bjerrum half integral method. (log $K_1/K_2 \geq 2.5$).

Since the difference between log k_1 and log k_2 was for less than 2.5. These values of the formation constants were refined to authenticate the data by following Irving & Rossotti procedure [9] (Table 2).

The system in reference had been defined too thermodynamically as the conditional formation constant equalled to thermodynamic constant under the applied conditions of infinite dilution and constant ionic strength. The ΔG values(s) for all the systems in reference assumed negative values giving enough reasons to believe the spontaneity of reaction between metal: Nd(III), Y(III) and the plant auxins : IAA, IPA, IBA.

Further the data registered a fall at higher temperature : 35^0C hinting on the less feasibility of these reactions at higher temperature. The calculations done on enthalpy change (ΔH) using the usual relations showed the assumption of high negative values by ΔH, indicating the possibility of the presence of covalency (a covalent bond between >NH and metal[10] in the metal chelates of all systems, and thus these reactions are enthalpy controlled.

The systems get favoured if the entropy change assumes positive value, but in the cases of the systems in reference the entropy change value was found negative which may ascribe to the solvent effects.

The thermodynamic and stability parameter of the systems under study are given in Table 2 and Table 3.

Table 2
Stability constants and thermodynamic parameters of systems involving Nd(III)-IAA, Nd(III)-IPA, and Nd(III)-IBA

System	Temp. (^{0}C))	log k_1	log k_2	log k_3	log β_3	k_2/k_1	k_3/k_2	ΔG^0 Kcal mol^{-1}	ΔH^0 Kcal mol^{-1}	ΔS^0 Cal mol^{-1} deg^{-1}
Nd(III) IAA	25	5.20 (5.25)	3.80 (3.90)	3.30 (3.35)	12.30 (12.50)	4.46×10^{-1}	2.81×10^{-1}	-17.04	-33.60	-55.51
	35	4.70 (4.70)	3.70 (3.70)	3.30 (3.30)	11.70 (11.70)	1.00×10^{-1}	3.98×10^{-1}	-16.50		
Nd(III) IPA	25	7.00 (7.00)	4.90 (4.90)	3.80 (3.85)	15.70 (15.75)	8.00×10^{-3}	9.00×10^{-2}	-21.47	-165.90	-484.74
	35	4.80 (4.80)	3.65 (3.65)	3.35 (3.35)	11.80 (11.80)	7.00×10^{-2}	5.01×10^{-1}	-16.63		
Nd(III) IBA	25	7.30 (7.30)	5.40 (5.40)	4.60 (4.70)	17.30 (17.40)	1.25×10^{-2}	1.99×10^{-1}	-23.72	-239.40	-723.70
	35	4.80 (4.80)	3.70 (3.70)	3.20 (3.20)	11.70 (11.70)	7.94×10^{-2}	3.16×10^{-1}	-16.50		

In parenthesis are the refined values.

Table 3
Stability constants and thermodynamic parameters of systems involving Y(III)-IAA, Y(III)-IPA, and Y(III)-IBA

System	Temp. (^{0}C))	log k_1	log k_2	log k_3	log β_3	k_2/k_1	k_3/k_2	ΔG^0 Kcal mol^{-1}	ΔH^0 Kcal mol^{-1}	ΔS^0 Cal mol^{-1} deg^{-1}
Y (III) IAA	25	5.80 (5.80)	4.00 (4.00)	3.50 (3.50)	13.30 (13.30)	1.58×10^{-2}	3.16×10^{-1}	-18.13	-67.20	-164.61
	35	4.70 (4.70)	3.70 (3.70)	3.30 (3.30)	11.70 (11.70)	1.00×10^{-1}	3.98×10^{-1}			
Y (III) IPA	25	5.30 (5.40)	3.80 (3.80)	3.30 (3.35)	12.40 (12.55)	2.50×10^{-2}	3.54×10^{-1}	-17.11	-69.30	-175.12
	35	4.20 (4.20)	3.50 (3.50)	3.20 (3.20)	10.90 (10.90)	1.99×10^{-1}	5.00×10^{-1}	-15.36		
Y (III) IBA	25	7.50 (7.50)	6.40 (6.40)	5.20 (5.25)	19.10 (19.20)	7.07×10^{-2}	7.08×10^{-2}	-26.18	-262.50	-793.00
	35	5.20 (5.20)	4.00 (4.05)	3.60 (3.70)	12.80 (12.95)	7.00×10^{-2}	3.54×10^{-1}	-18.25		

In parenthesis are the refined values.

References

[1]. S. S. Sawhney, G. S. Chauhan and Naresh Chandra, Thermochimcia Acta, 144 (1989), 173-175
[2]. S. S. Sawhney and G. S. Chauhan, Thermochimica Acta, 196 (1992), 477.
[3]. Man Mohan Singh Jassal and Susmita Yadav, Asian Journal of Chemistry, 24 (7), 2012, 3251-3252.
[4]. Y. Daijiro and I. Naomichi, Meiji Daiaka Nogakuka, 9 (1959) 19.
[5]. D. Cohen, B. L. Ginzhurg and C. H. Werguin Nature, 181 (1958), 686.
[6]. J. Bjerrum, Metal Ammine Formation in Aqueous Solution, Hasse Copenhagen, 1941, 298.
[7]. L. G. Van Uitert and L. G. Hass, J. Am. Chem. Soc., 75 (1953), 451
[8]. D. J. Pietrzk and C. W. Frank, Analytical Chemistry, Academic Press, INC, New York, Second Edition (1979), 149.
[9]. H. Irrvin, H. Rossotti, J. Chem. Soc., (1954), 2904-2910.
[10]. A. A. Kamneve, A. G. Shchelochkov, Yu. D. Perfiliev, Journal of Molecular Structure 56-3-564 (2001).
[11]. Josua Carvalho, Pierre Nottelet et.al. Biochimie 135 (2017) 186-195.