

PH-METRIC ANALYSIS AND THERMODYNAMIC PARAMETERS OF EU(III)-NAA, Gd(III)-NAA AND Tb(III)-NAA SYSTEMS

Gambhir Sing Chauhan,

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

Abstract

Varying opinions have been expressed on the mode of action of plant auxins activities (1-5) studied some metal-plant auxin systems in solution and solid state favouring chelation as a possible mode of action of plant auxin; their views are contrary to what has been expressed by Jenson (6). The affinity of metals to plant auxins, Sawhney, Chauhan and Co-workers [7-13] has been by different systems involving Trivalent metals: Eu, Gd, Tb and plant auxin: NAA have been taken as model studies; highlighting their solution chemistry, synthesis, decomposition mechanism, under thermodynamic conditions.

INTRODUCTION

Botanists are faced with native of interaction of plant auxins with metal ions present in soil : they have been confused for a long time. The first comment on the subject came from Koepfli, Themann and Went [14]. The conclusion based upon the investigation on the number of compounds had tally with the presence of a ring system with at least one double bond with side chain carrying a carboxyl group, and there being at least one carbon atom between the ring and carboxylic groups in an active growth substance. The subsequent results collected by Health and Clark [15] were to the contrary. Without recourse to experimentation, they suspected the plant auxins to act as chelating agents and chelation as possible mode of action for plant auxins. Highlight of the work oata and coworkers [16] 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). The system, on which the decision to build on was taken, are

- a. Eu – NAA
- b. Gd – NAA
- c. Tb – NAA

EXPERIMENTAL

All Chemical used were of analytical grade.

Reagents

HNO₃ : 0.1 M(aq), Ligand : IBA
 KNO₃ : M(aq), Solvent : 50%
 Dioxane
 NaOH: 0.1 M(aq),
 Metal Salt X(NO₃)₃.6H₂O (X = Eu, Gd, Tb).

Apparatus

MH Digital pH-Meter

RESULTS AND DISCUSSION

The complete study was done in 50% Dioxane in water and constant ionic strength (0.02M KNO₃). All experiments were performed at near infinite dilution so that the activity coefficient of species in solution were reduced to unity and thereby, the conditions were thermodynamically true. The protonation constants ($P^{\text{K}^{\text{H}}}$) of NAA were calculated for two different temperature using the equation of Henderson and Hesselback [17] and Irving and Rossetti (18) : 5.60 (25^oC) and 4.70 (35^oC). The value of \bar{n} was approximate 3 for the Eu(III)-NAA, Gd(III)-NAA and Tb(III)-NAA systems indicating the present of 1:1, 1:2 and 1:3 complex species in solution.

The metal ligand curves were well separated from the ligand curves, implying the replacement of the hydrogen atom of the carboxylic group in complexation. The strength of the NAA-metal bond decreased with the successive

attachment of the ligands (NAA) molecule ($\log K_1 > \log K_2 > \log K_3$) as is evident from the data given in Table 1. Which were determined using a graphical approach.

Table 1 : The stability constants and thermodynamic parameters of the Eu(III)-NAA, Gd(III)- NAA and Tb(III) – NAA systems:

Systems	Temp. °C	log					ΔG	ΔH	ΔS
		K_1	K_2	K_1/K_2	K_3	β_3			
Eu(III) - NAA	25	3.68 (3.66)	3.21 (3.20)	0.47	2.99 (2.99)	9.88 (9.85)	-13.43	-2. 20	
	35	3.70 (3.70)	3.22 (3.20)	0.48	3.00 (3.00)	9.92 (9.90)	-13.50		+13.68
Gd(III)- NAA	25	3.74 (3.73)	3.22 (3.21)	0.52	3.00 (2.99)	9.96 (9.96)	-13.54	-2. 94	
	35	3.70 (3.67)	3.22 (3.21)	0.48	2.99 (2.96)	9.86 (9.84)	-13.47		+34.12
Tb(III)- NAA	25	3.72 (3.71)	3.31 (3.22)	0.41	2.00 (3.00)	10.01 (9.92)	-13.67	-1.68	
	35	3.69 (3.68)	3.22 (3.21)	0.47	3.00 (2.99)	9.91 (9.88)	-13.47	-1.68	+38.28

a values in parenthesis are obtained due to graphical method ΔG and ΔH in KCal.mol⁻¹; ΔS in Cal.mol⁻¹, oC⁻¹

The Bejerrum method [19] could not be used to determine the bond strengths because the data obtained did not satisfy the basic conditions of the method ($\log K_1/K_2 \geq 2.5$). The above energy sequence favour lower temperature as a necessary condition for the completion reaction because of the consequent decrease in number of collisions with the decrease in Kinetic energy of the molecules involved.

Evidence of the spontaneity of the reactions could be found in the negative ΔG^0 values which become less negative at high temperatures in the Eu(III)-NAA, Gd(III)-NAA and Tb(III)-NAA systems making the formation of these systems less feasible with increasing temperatures ΔH^0 values show that the reaction are endothermic which is in agreement with the conclusions drawn previously on the systems, whereas an increase in the entropy ($+\Delta S^0$)

of the Eu(III)-NAA, Gd(III)-NAA and Tb(III)-NAA Systems implies spontaneity of the reaction. All work was carried out at infinite dilution, at which only mononuclear species are formed. The homogeneity was not observed in 50%D/W solvent (50% Dioxane(D) in water (W) throughout the pH- metric. The Eu(III) -NAA, Gd(III) -NAA and Tb(III) -NAA, reaction are accompanied by an increase of entropy ($+\Delta S$) and tend to be spontaneous (see Table 1).

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