

EQUILIBRIUM ANALYSIS AND THERMODYNAMICS STABILITY CONSTANT OF Eu (III)-IPA, Gd (III)-IPA, Tb (III)-IPA AND Dy (III)-IPA SYSTEMS

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ABSTRACT

Equilibrium analysis of Eu(III)-IPA, Gd(III)-IPA, Tb(III)-IPA and Dy(III)-IPA systems at constant ionic strength (1,0.02M KNO₃) and infinite dilution, meeting the conditions of thermodynamics environmental and the existence of mononuclear species in solution, has been performed in solution Potentiometrically. The stability and thermodynamics of the systems involved are discussed. The mode of action of plant auxins has been a controversial subject of metal complexes, which have the wide spectrum of applications beginning with analytical chemistry and ending with medicinal chemistry. Sawhney, Chauhan and Co-workers [1-14] have studied the affinity of metals to plant Auxins (IPA) highlighting their solution chemistry, synthesis, decomposition mechanism and kinetics. This paper reports on an extension of these studies on the interaction of the metal Eu(III), Gd(III), Tb(III) and Dy(III) with plant Auxins (IPA) in solution.

INTRODUCTION

Botanists are faced with nature 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 [15]. 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 [16] 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 [17] 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). This time some different systems involving plant auxin, IPA and trivalent -metals Eu,

Gd, Tb and Dy have been taken as model studies under thermodynamic conditions.

EXPERIMENTAL

All Chemical used were of analytical grade. The Procedure followed for the stability of the metals-IPA systems also described her. A Beckman PH-Metric equipped with glass and Calomel electrode was used.

Reagents

HNO₃ : 0.1 M(aq), Ligand : IBA

KNO₃ : M(aq), Solvent : 50% Dioxane

NaOH: 0.1 M(aq), Metal Salt : Tb(NO₃)₃.6H₂O

RESULTS AND DISCUSSION

The whole 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 (pK^H) of IBA were calculated for two different temperatures using the equation of Henderson and Hesselback (18): 5.45 (25°C) and 4.80 (35°C). The value of \bar{n} was approximately 3 for the Eu(III)-IPA, Gd(III)-IPA, Tb(III)-IPA and Dy(III)-IPA 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, empling the replacement of the hydrogen atom of the carboxylic group in complexation. The strength of IPA (Indole-3-Propionic acid) and metals Eu(III), Gd(III), Tb(III) and Dy(III) bond decreased with the successive attachment of the ligand (IPA) molecules ($\log K_1 > \log K_2 > \log K_3$) as is evident from the data given in Table 1. Which were determined using a graphical approach.

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

Systems	Temp. °C	log					ΔG	ΔH	ΔS
		K_1	K_2	K_1/K_2	K_3	β_3			
Eu(III)-IPA	25	3.76 (3.75)	3.20 (3.20)	0.56	3.00 (2.99)	9.96 (9.94)	-13.55	-2.52	
	35	3.70 (3.70)	3.20 (3.21)	0.49	2.98 (2.98)	9.89 (9.88)	-13.47		+35.55
Gd(III)-IPA	25	3.70 (3.80)	3.20 (3.18)	0.47	2.98 (2.94)	9.92 (9.93)	-13.54	-1.26	
	35	3.73 (3.71)	3.22 (3.20)	0.51	2.99 (2.99)	9.94 (9.90)	-13.50		+39.74
Tb(III)-IPA	25	3.70 (3.68)	3.23 (3.22)	0.47	2.99 (2.98)	9.92 (9.88)	-13.48	-1.68	
	35	3.70 (3.69)	3.20 (3.19)	0.50	2.98 (2.96)	9.88 (9.84)	-13.47		+38.38
Dy(III)-IPA	25	3.75 (3.73)	3.21 (3.20)	0.54	2.99 (3.00)	9.95 (9.93)	-13.54	-4.20	
	35	3.84 (3.82)	3.26 (3.22)	0.58	3.00 (2.99)	10.10 (10.03)	-14.14		+32.27

Values in parenthesis are obtained due to graphical method ΔG and ΔH in KCal.mol⁻¹; ΔS in Cal.mol⁻¹°C⁻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 complexation 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)-IPA, Gd(III)-IPA, Tb(III)-IPA and Dy(III) systems making the formation of these systems less feasible with increasing temperatures, the reverse was observed for the Tb(III) -IPA system. The negative 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) - IPA, Gd(III)-IPA Tb(III)-IPA and Dy(III)-IPA Systems implies spontaneity of the reaction.

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