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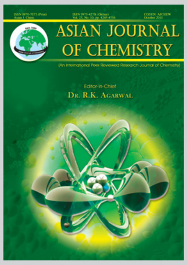

NOTE

Equilibrium Analysis of Ce(III)-Indole Derivative Systems

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This paper reports on equilibrium analysis of Ce(III)-indole-3-acetic acid, Ce(III)-indole-3-propionic acid, Ce(III)-indole-3-butyric acid systems at constant ionic strength (I, 0.1M KNO_3) and at infinite dilution. 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.

Key Words: Indole derivatives, Equilibrium analysis, Metal complex/chelates, Ionic strength, Thermodynamic stability.

A large amount of work on the assimilation of plant auxins by the plants has been done[1-5], but the controversy continues regarding whether plants assimilate the auxins as metal salts or metal complexes or chelates. All the plant auxins under study for their affinity to metal are monoprotic acids, having different molecular weights and titrable hydrogen one, which is removable with the introduction of hydroxyl ion into the plant auxin solution. The positional status of carboxylic and -NH groups on the surfaces of indole-3-acetic acid (IAA), indole-3-propionic acid (IPA) and indole-3-butyric acid (IBA) molecules sign both the possibilities of salt formation and complexation when these molecules are brought in contact with the metal ion in the solution under thermodynamic conditions[6]. This report is an attempt to contribute knowledge of the metal affinity to plant auxins in solution, carrying equilibrium analysis of Ce(III)-IAA, Ce(III)-IPA and Ce(III)-IBA, systems and give an explanation of the structure, stability and thermodynamics of these systems.

The chemicals 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. The metal contents were estimated by standard methods.

For solution studies, solutions having identical concentrations of the common ingredients in different sets were prepared as recommended by Bjerrum and Calvin[7]. The pH was corrected for non-aqueous media (50 % v/v 1,4-dioxane/distilled water) according to Van Uitert and Haas[8] and was measured on a Toshniwal pH-meter, model CL-54 with sensitivity of ± 0.5 was duly standardized with the suitable buffers. The ionic strength was maintained at 0.1 M KCl. The homogeneity and the clarity of the solutions were maintained throughout the experimental time.

The sets of solutions necessary for leading us to the values of equilibrium factors were prepared as termed as (A), (B) and (C). (A) 2×10^{-3} M HNO_3 + 1×10^{-1}M KNO_3; (B) 2×10^{-3} M HNO_3 + 1×10^{-1}M KNO_3 + 20×10^{-4} M ligand (plant auxin); (C) 2×10^{-3}M HNO_3 + 1×10^{-1}M KNO_3 + 20×10^{-4} M ligand (plant auxin) + 2×10^{-4} M Ce(III).

The sets (A), (B) and (C) were titrated using 1×10^{-1} NaOH as titrant pH-metrically at two temperatures (25 and 35 ºC). The curves (pH *vs* base) obtained were of usual shape.

pH Curves displaying the separation of metal-ligand 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 in IAA, IPA or IBA, which has a potential to form metal complexes.

Examination of the formation curves ($\bar{n}$ *vs* pL; the formation functions were calculated following the usual Bjerrum procedure) indicated that the stepwise formation tended to decrease, concluding a weakening of bond strength with the successive addition of the ligand molecules (IAA, IPA, IBA) to the metal (C_e).

The $\bar{n}$ values was found to be nearly 3 suggesting the three types of complexes were formed 1:1, 1:2, 1:3 under experimental conditions. The liberation of protons under the limiting conditions of a 1:4 mixture (metal/ligand) demonstrated the above results. Protonation constants of Ce(III)-plant auxin systems are presented in Table-1. The protonation constants of IAA, IPA, IBA could be worked out by applying the concepts of Henderson[9] and Irving and Rossotti[10].

TABLE-1
PROTONATION CONSTANTS OF PLANT AUXINS

Plant auxin	log $^{P}k^{H}$	
	25 ºC	35 ºC
Indole-3-acetic acid	6.40	6.10
Indole-3-propionic acid	6.60	6.30
Indole-3-butyric acid	7.10	6.80

Chemical analysis also showed that one mole of Ce(III) combined with three moles of plant auxins (IAA, IPA, IBA). Further pH-metric titration revealed the release of proton during complexation in all three systems; the reaction may be represented as:

$$Ce^{3+} + LH \rightleftharpoons CeL^{2+} + H^{+}$$
$$CeL^{2+} + LH \rightleftharpoons CeL_2^{+} + H^{+}$$
$$CeL^{+} + LH \rightleftharpoons CeL_3 + H^{+}$$

Here, LH = ligand shown with removable hydrogen. The thermodynamic and stability parameters of the systems under study are given in Table-2.

TABLE-2
STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF THE SYSTEMS Ce(III)INDOLE-3-ACETIC ACID, Ce(III)INDOLE-3-PROPIONIC ACID AND Ce(III)INDOLE-3-BUTYRIC ACID (50 % AQUEOUS DIOXANE, 0.1 M KNO_3 IONIC STRENGTH)

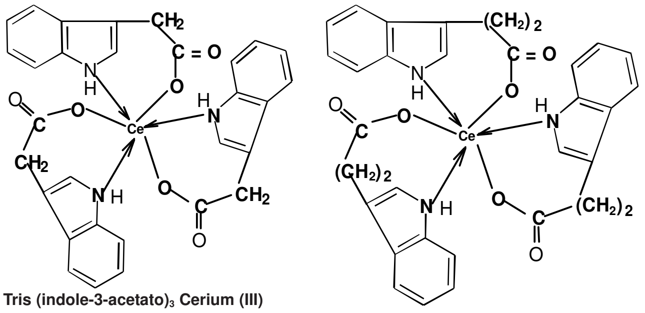
Stability constants	Temperature (ºC)		ΔGº (kcal mol^{-1})		ΔHº (kcal mol^{-1})	ΔSº (cal mol^{-1} deg^{-1})
	25 ºC	35 ºC	25 ºC	35 ºC		
Ce(III)-indole-3-acetic acid						
log k_1	5.70	4.60				
log k_2	4.20	3.60				
log k_1	3.50	3.20				
log β_3	13.40	11.80	-18.47	-16.67	-73.50	-184.60
Ce(III)-indole-3-propionic acid						
log k_1	6.00	4.80				
log k_2	4.30	4.00				
log k_1	3.60	3.55				
log β_3	13.90	12.40	-19.16	-17.47	-69.30	-168.27
Ce(III)-indole-3-butyric acid						
log k_1	6.70	6.00				
log k_2	5.10	3.90				
log k_1	4.10	3.30				
log β_3	15.90	13.20	-21.68	-18.60	-69.25	-168.20

Table-1 shows a decreasing trend in the values of $^{P}k^{H}$. Stepwise formation constants $k_1 > k_2 > k_3$ (*cf.* Table-2) for the Ce(III)-plant auxin systems with the rise in temperature suggesting the low temperature as a favourable condition for metal complexation with IAA/IPA/IBA under optimal conditions in non-aqueous media due to lowering of collisions among the molecules with decrease of kinetic energies of the molecules involved.

The ΔGº value(s) for the systems in reference assumed negative values giving enough reasons to believe the spontaneity of reaction between metal Ce (III) and the plant auxins: IAA, IPA, IBA.

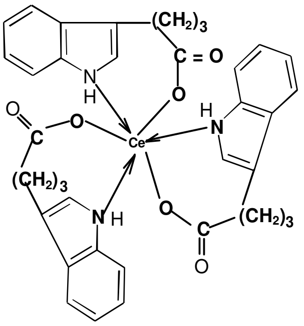
Further the data registered a fall at higher temperature: 35 ºC hinting on the less feasibility of these reactions at higher temperature. The calculations done on enthalpy change (ΔHº) using the usual relations showed the assumption of high negative values by ΔH^0, indicating the possibility of the presence of covalence (a covalent bond between >NH and metal)[8] in the metal chelates of all the 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. In light of solution data, the metal Ce(III) in these complexes may be visualized as shown in **Scheme-I**.



Tris (indole-3-acetato)$_3$ Cerium (III)

Tris (indole-3-propionato)$_3$ Cerium (III)



Tris (indole-3-butyrato)$_3$ Cerium (III)

Scheme-I

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