Thermochimica Acta, 196 (1992) 477–481
Elsevier Science Publishers B.V., Amsterdam

Equilibrium analysis of Dy(III). Plant auxin systems

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(Received 7 June 1991)

Abstract

Equilibrium analysis of Dy–IBA, Dy–IPA and Dy–NAA systems at constant ionic strength (I, 0.02 M KNO_3) and at infinite dilution, meeting the conditions of thermodynamic environment and the existence of mononuclear species in solution, has been performed in solution potentiometrically. The stability and thermodynamics of the systems involved are discussed.

INTRODUCTION

In spite of advances, critiques and countercritiques on the mode of action of plant auxins, the controversy on this issue still hangs on. Sawhney et al. [1–4] have contributed greatly to knowledge of metal affinity to plant auxins in solution and in the solid state. This is an attempt to carry out an equilibrium analysis of Dy(III)–plant auxin (indole-3-butyric acid (IBA), indole-3-propyric acid (IPA), 1-naphthalene acetic acid (NAA)) systems and to give an explanation of the stability and thermodynamics of these systems.

EXPERIMENTAL

The chemicals used were of analytical grade. The instrumental and experimental conditions described in earlier reports [2] have been kept here.

RESULTS AND DISCUSSION

Within a thermodynamically true environment attainable at infinite dilution and constant ionic strength (0.1 M KNO_3) the pH titration was performed. IBA, IPA and NAA contain a titratable H^+ as a consequence of ionisation of the carboxylic group making the study of these systems possible. The protonation constants of IPA, IBA, NAA (Table 1) could be worked out by applying the concepts of Henderson [5] and Irving and Rossotti [6].

TABLE 1

Protonation constants of IBA, IPA and NAA

Auxin	log P_KH	
	25 °C	35 °C
IBA	5.60	5.10
IPA	5.45	4.80
NAA	5.60	4.70

All work was carried out at infinite dilution, at which only mononuclear species are formed, and so could meet the basic conditions of the Bjerrum technique [7]. Inhomogeneity was not observed in 50% D/W solvent (50% dioxane (D) in water (W)) throughout the pH titration (Fig. 1).

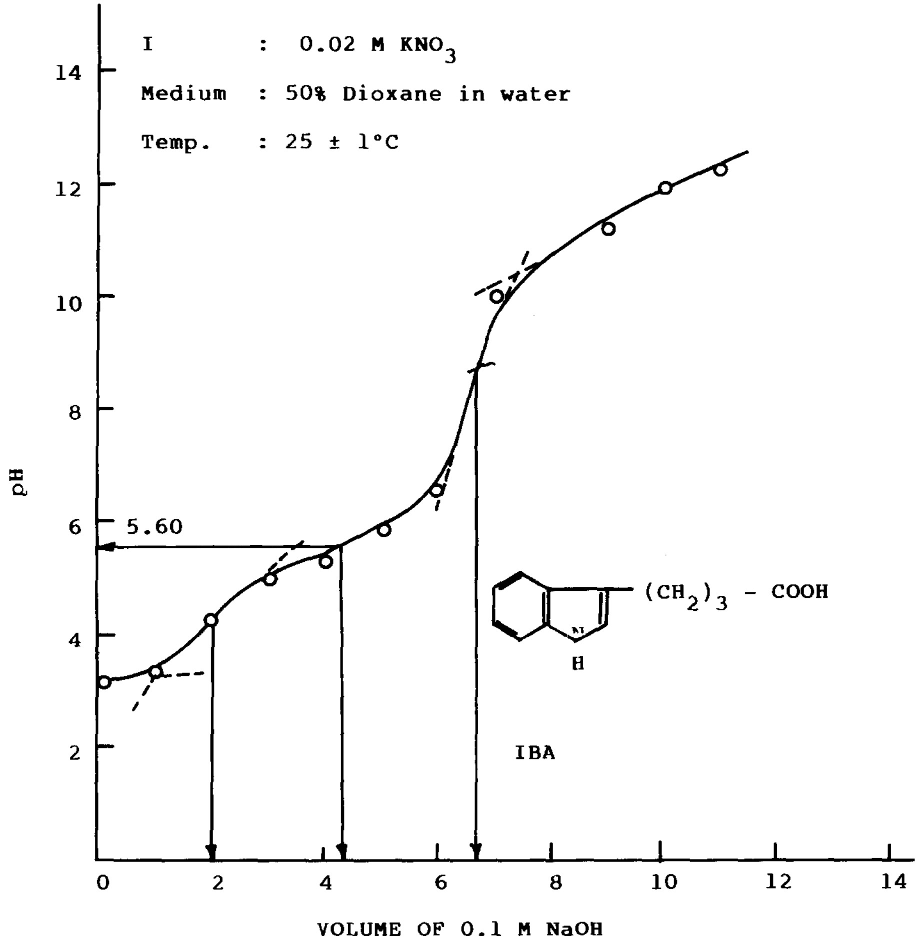


Fig. 1. Potentiometric titration of IBA+HNO_3 with NaOH.

TABLE 2

Stability constants and thermodynamic parameters of the Dy(III)–IBA, Dy(III)–IPA and Dy(III)–NAA systems [a]

System	Temp. (°C)	$\log k_1$	$\log k_2$	$\log (k_1/k_2)$	$\log k_3$	β_3	ΔG (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} $°\mathrm{C}^{-1}$)
Dy–IBA	25	3.72	3.22	0.50	3.00	9.94	−13.80	−2.52	
		(3.72)	(3.23)		(3.00)	(10.12)			
	35	3.84	3.26	0.58	2.99	10.09	−14.01		+37.37
		(3.82)	(3.24)		(2.88)	(9.44)			
Dy–IPA	25	3.75	3.21	0.54	2.99	9.95	−13.54	−4.20	
		(3.73)	(3.20)		(3.00)	(9.93)			
	35	3.84	3.26	0.58	3.00	10.10	−14.14		+32.27
		(3.82)	(3.22)		(2.99)	(10.03)			
Dy–NAA	25	4.76	3.38	0.38	2.99	11.13	−14.28	−12.18	
		(4.18)	(3.31)		(2.98)	(10.47)			
	35	4.09	3.21	0.88	2.94	10.24	−14.35		+7.05
		(4.05)	(3.20)		(2.93)	(10.18)			

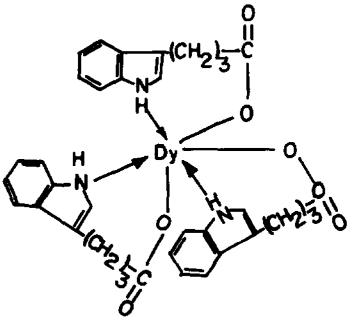
[a] Values in parentheses are obtained by the graphical method.

The ligand number ($\bar{n}$) and free ligand exponent (pL) were calculated following Bjerrum's concept. The $\bar{n}$ of the systems Dy–IPA, Dy–IBA and Dy–NAA was close to 3 demonstrating the presence of 1:1, 1:2 and 1:3 species in solution. From formation curves of the systems ($\bar{n}$ versus pL), the ratio of stepwise formation constants, i.e. $\log k_1/k_2$ fell below the value $\geqslant 2.5$, which is basic to the applicability of the method in the estimation of metal ligand formation constants. To provide sense and meaning to the constants, the graphical method was adopted according to the following equation:

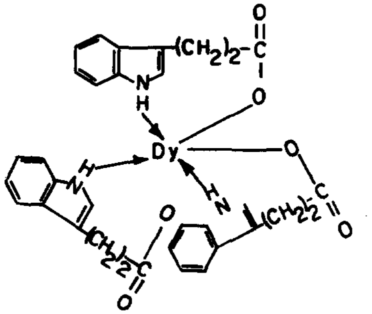
$$\log k_n = \mathrm{pL} + \log \frac{\bar{n} - (n-1)}{(n - \bar{n})}$$

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 IPA, IBA and NAA.

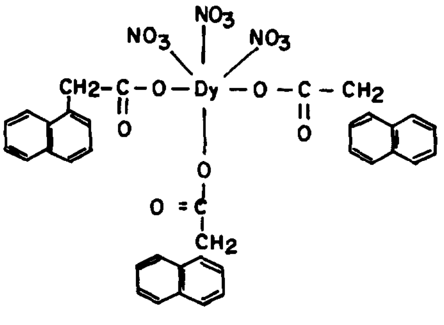
In the Dy–NAA system the values of $\log k_1$, $\log k_2$ and $\log k_3$ decreased with increasing temperature favouring a low temperature for complexation; this appears to be due to the decrease in the number of collisions with the decrease in kinetic energy of the molecules involved in the reaction. In other systems, Dy–IBA and Dy–IPA, log k_1 and log k_2 values increased as the temperature rose, whereas a slight decrease in the log k_3 value was observed under these conditions. The reactions between Dy and IBA, IPA or NAA are spontaneous as indicated by the negative ΔG value; their feasibility increased as evinced by the increased negativity



Tris (indole —3—butyrato) Dysprosium (3 +)



Tris (indole —3—propyrato) Dysprosium (3+)



Tris (1—Naphthalene acetata) Dysprosium (3+)

Scheme 1.

of ΔG at higher temperature. The exothermic nature of these reactions could be based upon negative ΔH values, which signalled the existence of covalency in Dy–plant auxin complexes. The Dy–IBA, Dy–IPA, Dy–NAA reactions are accompanied by an increase of entropy (positive ΔS) and tend to be spontaneous (see Table 2).

This study indicates that the structures shown in Scheme 1 appear to be the only possibilities.

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