Thermochimica Acta, 115 (1987) 375–380
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

AFFINITY OF PLANT AUXINS IAA, IBA, IPA AND NAA TO METALS

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(Received 10 September 1986)

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 [1–3]. Jensen [4] expressed other opinions on the issue. Research has been initiated to resolve the puzzle and to arrive at some conclusion. This contribution is devoted to the solution study of the systems involving either IAA, IPA, IBA or NAA with either Ce(III), Pr(III), Nd(III) or Sm(III), considering the determination of stoichiometries, stability constants and thermodynamics of the systems and their explanation.

EXPERIMENTAL

All the ligands and metal salts used were of analytical grade. The whole study has been carried out in 50% aqueous acetone at an ionic strength of 0.01 M KNO_3. Three sets were prepared and pH-metrically titrated against 0.1 M NaOH (50% aqueous acetone): (a) 4.00×10^{-3} M HNO_3, 1.00×10^{-2} M KNO_3; (b) 4.00×10^{-3} M HNO_3, 1.00×10^{-2} M KNO_3, 20.00×10^{-4} M auxin; (c) 4.00×10^{-3} M HNO_3, 1.00×10^{-2} M KNO_3, 20.00×10^{-4} M auxin, 4.00×10^{-4} M metal ion. The ratio of metal/auxin concentrations was maintained at 1 : 5 in order to satisfy the highest ligancy.

A Beckman pH-meter equipped with glass and calomel electrodes was used to record pH value. Each pH value was corrected for volume, and a correction due to Van Uitert and Haas [5] for non-aqueous media was applied.

RESULTS AND DISCUSSION

Plant auxins are monoprotic (I–IV). Protonation constants ($^{P}K^{H}$) of auxins were determined following the Henderson and Hesselback equation [6], which reduces to $pH = pK = \log {}^{P}K^{H}$ at half neutralization; a sample plot is shown in Fig. 1 (Table 1).

0040-6031/87/$03.50

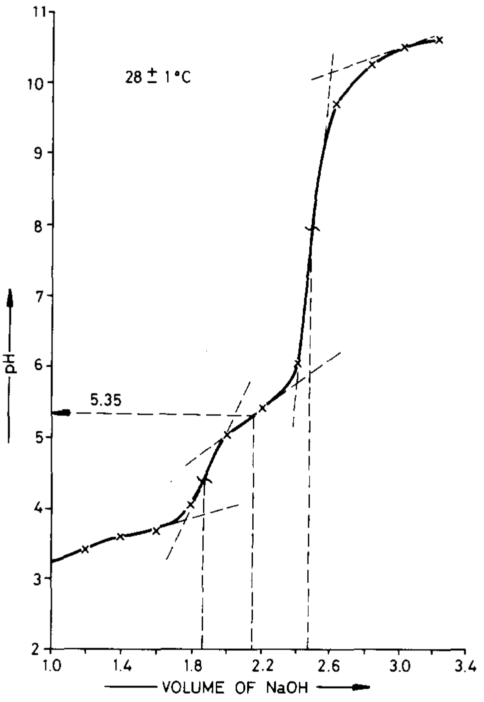


Fig. 1. pH-metric titrations of solution of a mixture of strong acid (HNO_3, 0.04 M) and a weak acid (IAA, 0.001 M) with 0.1 M NaOH medium: 50% acetone in water, ionic strength 0.01 M KNO_3.

The metal–auxin stability constants were evaluated following Bjerrum's concept [7]. The systems as shown by formation curves (n vs. pL) could not acquire the condition necessary for Bjerrum half integral method [7] ($\log k_1/k_2 \geqslant 2.5$), since the difference between $\log k_1$ and $\log k_2$ was far less than 2.5. To make the data more reliable, pointwise calculation and graphical methods, reported earlier by Sawhney et al. [8,9], were applied (Table 2).

TABLE 1

Protonation constants of plant auxins

Auxin	$\log {}^{P}K^{H}$	
	28 °C	38 °C
IAA	5.35	5.00
IBA	6.05	5.30
IPA	6.10	5.40
NAA	5.80	4.75

TABLE 2

Stability constants and thermodynamic parameters of systems involving Nd(III), Pr(III), Ce(III), Sm(III) and IAA, IBA, IPA and NAA

Temp. (°C)	log K_1 [a]	log K_2 [a]	log K_1/K_2	log K_3 [a]	log β_3	ΔG (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} °C^{-1})
Nd(III)-IAA								
28	4.66	3.49		3.26	11.41	−15.72		
	(4.65	(3.60)	1.05	3.28				
							47.55	
38	5.20	3.99		3.33	12.52	−17.82		210.18
	(5.18)	(3.90)	1.28	(3.31)				
Pr(III)-IAA								
28	4.80	3.97		3.20	11.97	−16.49		
	(4.75)	(3.95)	0.80	(3.30)				
							10.71	
38	4.84	3.97		3.41	12.22	−17.39		90.35
	(4.77)	(3.95)	0.82	(3.30)				
Ce(III)-IAA								
28	4.69	3.80		3.30	11.79	−16.24		
	(4.62)	(3.97)	0.65	(3.30)				
							24.85	
38	5.00	4.07		3.30	12.31	−17.60		136.49
	(4.95)	(4.00)	0.95	(3.30)				
Sm(III)-IAA								
28	5.38	3.94			09.32	−12.84		
	(5.25)	(3.88)	1.37					
							−67.68	
38	4.18	3.56			07.74	−11.02		−182.23
	(4.05)	(3.53)	0.52					
Nd(III)-IBA								
28	4.80	4.15		3.26	12.21	−16.82		
	(4.80)	(4.15)	0.70	(3.33)				
							12.85	
38	4.99	4.17		3.35	12.51	−17.80		98.56
	(4.93)	(4.10)	0.83	(3.30)				
Pr(III)-IBA								
28	5.16	3.93		3.34	12.43	−17.12		
	(5.13)	(3.90)	1.23	(3.30)				
							−38.55	
38	4.54	3.83		3.16	11.53	−16.41		−71.20
	(4.48)	(3.73)	0.75	(3.28)				
Ce(III)-IBA								
28	5.03	3.72		3.34	12.09	−16.65		
	(4.95)	(3.60)	1.35	(3.30)				
							−13.71	

TABLE 2 (continued)

Temp. (°C)	log K_1 [a]	log K_2 [a]	log K_1/K_2	log K_3 [a]	log β_3	ΔG (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} $°C^{-1}$)
38	5.03	3.66		3.08	11.77	−16.75		9.78
	(5.05)	(3.60)	1.45	(3.33)				
Sm(III)-IBA								
28	5.19	4.16			9.35	−12.88	−56.97	
	(5.15)	(4.10)	1.05					
38	4.42	3.60			8.02	−11.41		−146.49
	(4.35)	(3.53)	0.82					
Nd(III)-IPA								
28	4.36	3.60		3.26	11.22	−15.45	31.27	
	(4.35)	(3.60)	0.75	(3.30)				
38	4.93	3.74		3.28	11.95	−17.01		155.23
	(4.88)	(3.63)	1.25	(3.30)				
Pr(III)-IPA								
28	4.26	3.70		3.23	11.19	−15.41	−12.85	
	(4.13)	(3.58)	0.55	(3.28)				
38	4.20	3.54		3.15	10.89	−15.50		8.51
	(4.13)	(3.58)	0.55	(3.33)				
Ce(III)-IPA								
28	4.72	3.70		3.35	11.77	−16.21	−29.99	
	(4.75)	(3.58)	1.17	(3.27)				
38	4.15	3.64		3.28	11.07	−15.75		−45.76
	(4.13)	(3.55)	0.58	(3.30)				
Sm(III)-IPA								
28	4.25	3.64			7.89	−10.99	57.40	
	(4.15)	(3.55)	0.60					
38	5.03	4.20			9.23	−13.14		226.81
	(5.00)	(4.23)	0.77					
Nd(III)-NAA								
28	4.18	3.60		3.39	11.17	−15.39	−5.14	
	(4.15)	(3.58)	0.57	(3.30)				
38	4.16	3.57		3.32	11.05	−15.73		34.04
	(4.12)	(3.55)	0.57	(3.30)				
Pr(III)-NAA								
28	4.78	3.70		3.39	11.87	−16.35	−35.98	
	(4.70)	(3.62)	1.07	(3.30)				
38	4.16	3.63		3.24	11.03	−15.70		−65.23
	(4.10)	(3.59)	0.51	(3.30)				

TABLE 2 (continued)

Temp. (°C)	log K_1 [a]	log K_2 [a]	log K_1/K_2	log K_3 [a]	log β_3	ΔG (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} $°C^{-1}$)
Ce(III)-NAA								
28	4.16	3.60		3.36	11.12	−15.32		
	(4.10)	(3.55)	0.55	(3.30)				
							−9.00	
38	4.08	3.53		3.30	10.91	−15.53		21.00
	(4.05)	(3.52)	0.53	(3.30)				
Sm(III)-NAA								
28	4.33	3.65		–	7.98	−10.99		
	(4.25)	(3.58)	0.67	–				
							−13.71	
38	4.06	3.60		–	7.66	−10.90		−9.02
	(4.05)	(3.52)	0.53	–				

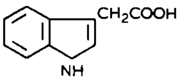
[a] Values in parentheses are from the formation curves of various systems.

In the systems involving Sm(III) and one of the plant auxins, n approached 2, justifying the presence of two complex species of 1 : 1 and 1 : 2 stoichiometries in solution. For the rest of the systems this value approached 3, indicating 1 : 1, 1 : 2 and 1 : 3 (metal/auxin) complex species in solution.

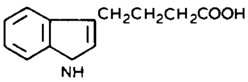
A close look at stepwise formation constants revealed a decreasing trend, i.e., $\log k_1 > \log k_2 > \log k_3$, evincing the decrease in strength of auxin–metal bonds with the successive attachment of the ligand molecules.

A clear separation of the metal–auxin curve from the auxin curve led us to believe in the involvement of the auxin's carboxylic group in complexation.

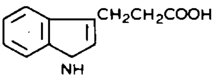
The study was carried out at near infinite dilution. Under these conditions the formation constant determined at any specific concentration becomes the thermodynamic formation constant since all the activity coefficients of the chemical species involved are equal to unity.



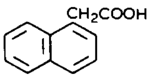
IAA
(I)



IBA
(II)



IPA
(III)



NAA
(IV)

In the systems Sm(III)–IAA; Pr(III)–, Ce(III)– and Sm(III)–IBA; Pr(III)– and Ce(III)–IPA; and Nd(III)–, Pr(III)–, Ce(III)– and Sm(III)–NAA, logarithmic values of k_1, k_2 and k_3 decreased with increasing temperature favouring a low temperature for complexation. A decreased number of collisions gives a decrease in kinetic energy of the molecules, and hence the stability is lowered with increasing temperature; in the remaining systems the reverse was observed. ΔG^0 values for all the systems are negative, indicating the spontaneity of the reactions. The reactions Nd–, Pr– and Ce–IAA; Nd– and Ce–IBA; Nd–, Pr– and Sm–IPA; and Nd– and Ce–NAA, were more feasible as this value became more negative at higher temperatures; the opposite was true of the other reactions. The reactions given at the start of this paragraph were endothermic whereas the rest of the reactions acquired positive ΔH^0 values making them exothermic in nature. These findings matched the conclusions drawn earlier on these systems. The reactions between Nd/Pr/Ce and IAA, Nd/Ce and IBA, Nd/Sm and IPA are accompanied by an increase of entropy ($+\Delta S^0$) and tend to be spontaneous; a decrease in entropy in other systems may be attributed to solvent effects.

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