

Stepwise Stability Constants & Thermodynamic Functions of In(III) Complexes with Some Substituted Derivatives of Quinoline & Pyridine

R. SARIN & K. N. MUNSHI

Department of Chemistry, New University Campus, Nagpur

Received 3 February 1976; accepted 22 July 1976

Stability constants of indium (III) complexes with 8-hydroxyquinoline, 8-hydroxy-2-methylquinoline (in 50% aq. dioxane) and with 8-hydroxyquinoline-5-sulphonic acid, 8-hydroxy-7-iodoquinoline-5-sulphonic acid, pyridine-2-carboxylic acid and pyridine-2,6-dicarboxylic acid (in aq. medium) have been determined using Calvin-Bjerrum pH-titration technique as modified by Irving and Rossotti. The log K values have been refined employing various computational methods. The stepwise changes in the free energy, enthalpy and entropy values for complexation reactions have been evaluated at three different temperatures.

COMPLEXES of In(III) with 8-hydroxyquinoline and some of its derivatives have been studied using spectrophotometric^{1,2}, solubility³ and solvent extraction methods⁴. However, the stability constants of the complexes have not been reported. We report here the stepwise metal-ligand stability constants of indium(III) complexes with 8-hydroxyquinoline (OX), 8-hydroxy-2-methylquinoline (MeOX), 8-hydroxyquinoline-5-sulphonic acid (OXSA), 8-hydroxy-7-iodoquinoline-5-sulphonic acid (OXISA), pyridine-2-carboxylic acid (PA) and pyridine-2,6-dicarboxylic acid (DPA). The stepwise free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) changes accompanying the complexation reactions have also been evaluated.

Materials and Methods

A stock solution (0.01M) of $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Schuchardt, Munich) was prepared in a calculated quantity of perchloric acid to prevent the hydrolysis. The In(III) content was determined gravimetrically⁵. 8-Hydroxyquinoline (AnalaR, BDH) and 8-hydroxy-2-methylquinoline (Eastman-Kodak) were recrystallized from aq. ethanol and the stock solutions (0.015M) prepared in purified dioxane⁶. 8-Hydroxyquinoline-5-sulphonic acid (Merck) and 8-hydroxy-7-iodoquinoline-5-sulphonic acid (BDH) were dried at 100° and their stock solutions (0.004M) prepared in doubly distilled water. These solutions were standardized by determining the equivalent weights of the acids. Stock solutions (0.025M) of pyridine-2-carboxylic acid (Koch-Light) and pyridine-2,6-dicarboxylic acid (Fluka) were prepared in doubly distilled water and standardized potentiometrically.

A pH-meter (Beckman model H-2) with a glass-calomel electrode assembly connected through agar bridge saturated with KNO_3 was used for pH measurements. Temperature was maintained using a thermostat having an accuracy of $\pm 0.2^\circ$. The titration cell was so designed that it enabled pH measurements in an atmosphere of nitrogen.

Procedure—Bjerrum-Calvin pH-titration technique^{7,8} was employed for which the following three

mixtures were prepared: (A) perchloric acid; (B) perchloric acid + ligand solution; (C) perchloric acid + ligand solution + metal salt solution. The concentrations of the common ingredients were identical in different mixtures. An appropriate amount of neutral sodium perchlorate (1.0M) was added to maintain the desired ionic strength. These mixtures were titrated against standard carbonate-free sodium hydroxide (1.0M) standardized potentiometrically against potassium hydrogen phthalate⁹. A graph between pH meter reading B and the volume of alkali added was plotted. The three titration curves obtained were referred to as acid titration curve (A), ligand titration curve (B), and complex titration curve (C).

Proton-ligand and metal-ligand stability constants

—The proton-ligand stability constants were computed as follows: The values of \bar{n}_A at various pH (B) values were calculated from the acid and ligand titration curves using the formula of Irving and Rossotti¹⁰. Calculation of the "practical" proton-ligand stability constants was carried out by plotting a graph of \bar{n}_A against pH (B) and then applying various computational methods¹¹.

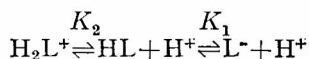
The stepwise stability constants of the metal complexes were determined by analysing the formation curves (\bar{n} versus pL) using various computational methods¹¹. The values of \bar{n} , the average number of ligands attached per metal ion, and the free ligand exponent pL were calculated from ligand and complex titration curves using the formula of Irving and Rossotti¹⁰.

Thermodynamic parameters—The values of the overall changes in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) for In(III) complexes have been calculated using the temperature coefficient and Gibbs-Helmholtz equation¹².

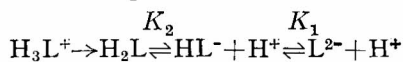
Results

"Practical" proton-ligand stability constants—The curves obtained from the function $\bar{n}_A(B)$ were extended between 0 and 2 in the \bar{n}_A scale for OX and MeOX. This showed that the dissociation of

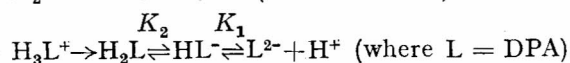
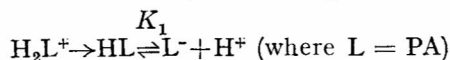
H₂L⁺ (where L = OX or MeOX) takes place as follows:



The curves obtained from the function \bar{n}_A (pH) were extended between 0 and 2 in the \bar{n}_A scale for OXSA and OXISA showing the complete dissociation of —SO₃H group present in both the ligands. Thus the dissociation of H₂L (where L = OXSA and OXISA) can be represented as follows:



The curves obtained from the function \bar{n}_A (pH) were extended from 0 to 1 for PA and from 0 to 2 for DPA. The results showed that pyridyl nitrogen in both the cases gets deprotonated at a very low pH value. This is in agreement with the results reported earlier for PA¹³ and DPA¹⁴. Thus, the dissociation of H₂L⁺ (where L = PA) and H₃L⁺ (where L = DPA) can be represented as follows:



The values of stepwise proton-ligand stability constants at various temperatures obtained by the method of interpolation at various \bar{n}_A values¹¹ are summarized in Table 1.

Metal-ligand stability constants — The nature of the formation curves (Fig. 1) for In(III)-OX, In(III)-MeOX, In(III)-OXSA, In(III)-OXISA and In(III)-PA shows the stepwise formation of three chelates. The values of log K₁, log K₂ and log K₃ were obtained from the formation curves at $\bar{n} = 0.5, 1.5$ and 2.5 respectively. But this method did not give reliable values as log K₁/K₂ and log K₂/K₃ < 3.0. Therefore, the values obtained by this method have been refined by (i) correction term method, (ii) graphical method and (iii) least-squares method¹¹. The mean values of stability constants at various temperatures having error limit of ±0.05 are summarized in Table 1.

The formation curves for In(III)-DPA show the stepwise formation of two chelates. The values of log K₁ and log K₂ for these chelates are summarized in Table 1.

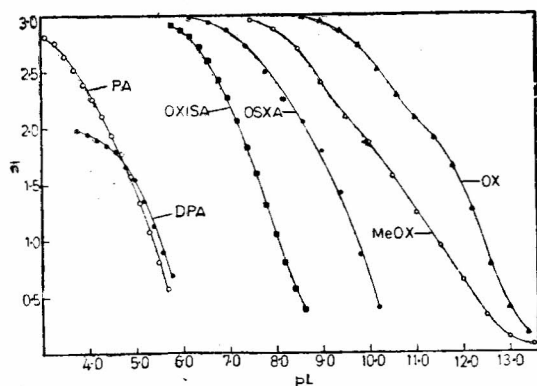


Fig. 1 — Formation curves of In(III) complexes with OX, MeOX, OXSA, PA and DPA

Thermodynamic parameters — Values of the stepwise changes in the free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), calculated at three different temperatures, have been summarized in Table 2.

TABLE 1 — "PRACTICAL" PROTON-LIGAND AND METAL-LIGAND STABILITY CONSTANTS

Constants	Temperature		
	25°	35°	45°
OX			
log K ₁ ^H	10.77	10.69	10.60
log K ₂ ^H	4.53	4.47	4.41
MeOX			
log K ₁ ^H	10.97	10.87	10.76
log K ₂ ^H	5.08	5.01	4.95
OXSA			
log K ₁ ^H	8.21	8.11	8.00
log K ₂ ^H	3.90	3.85	3.80
OXISA			
log K ₁ ^H	6.82	6.74	6.66
log K ₂ ^H	2.50	2.47	2.44
PA			
log K ₁ ^H	5.30	5.18	5.05
DPA			
log K ₁ ^H	4.48	4.39	4.29
log K ₂ ^H	2.06	2.03	2.00
In(III)-OX			
log K ₁	12.66	12.55	12.42
log K ₂	12.17	12.04	11.89
log K ₃	10.26	10.08	9.88
In(III)-MeOX			
log K ₁	12.30	12.22	12.12
log K ₂	10.51	10.40	10.27
log K ₃	8.86	8.73	8.60
In(III)-OXSA			
log K ₁	9.80	9.70	9.61
log K ₂	9.60	9.51	9.41
log K ₃	7.82	7.70	7.60
In(III)-OXISA			
log K ₁	8.27	8.20	8.12
log K ₂	7.85	7.77	7.70
log K ₃	6.85	6.67	6.59
In(III)-PA			
log K ₁	5.56	5.44	5.34
log K ₂	5.14	5.01	4.90
log K ₃	3.82	3.74	3.64
In(III)-DPA			
log K ₁	5.82	5.73	5.63
log K ₂	5.21	5.10	5.01

TABLE 2 — VALUES OF THERMODYNAMIC PARAMETERS

Reaction step	ΔG (kcal/mole) at			ΔH (kcal/mole) at 35°	ΔS (e.u.) at 35°
	25°	35°	45°		
In(III)-OX					
$n = 1$	-17.26	-17.69	-18.16	-4.9	+42
$n = 2$	-16.60	-16.97	-17.30	-5.7	+36
$n = 3$	-13.99	-14.21	-14.37	-7.7	+21
In(III)-MeOX					
$n = 1$	-16.77	-17.23	-17.64	-3.7	+44
$n = 2$	-14.33	-14.66	-14.95	-4.9	+32
$n = 3$	-12.08	-12.30	-12.51	-5.3	+26
In(III)-OXSA					
$n = 1$	-13.36	-13.66	-13.98	-3.6	+33
$n = 2$	-13.08	-13.40	-13.69	-4.5	+29
$n = 3$	-10.65	-10.85	-11.06	-5.3	+18
In(III)-OXISA					
$n = 1$	-11.28	-11.55	-11.81	-2.8	+28
$n = 2$	-10.70	-10.95	-11.20	-3.2	+25
$n = 3$	-9.20	-9.40	-9.60	-3.2	+20
In(III)-PA					
$n = 1$	-7.57	-7.66	-7.77	-4.5	+10
$n = 2$	-7.01	-7.06	-7.13	-4.9	+7
$n = 3$	-5.21	-5.27	-5.30	-3.7	+5
In(III)-DPA					
$n = 1$	-7.93	-8.08	-8.19	-3.7	+14
$n = 2$	-7.10	-7.19	-7.29	-4.1	+10

The precision of ΔG values is ± 0.8 kcal mole⁻¹, ΔH values ± 1.0 kcal mole⁻¹ and ΔS values is ± 2.0 cal deg⁻¹ mole⁻¹.

Discussion

It is clear from Table 1 that In(III)-OX complexes are more stable than In(III)-MeOX complexes, though on the basis of basicity considerations alone, MeOX complexes should have been more stable. This anomaly may be due to steric hindrance caused by the methyl group.

In(III)-OXISA complexes are less stable than In(III)-OXSA due to lower basicity of OXISA as a result of electron-withdrawing iodo group.

The greater stability of In(III)-DPA complexes as compared with that of In(III)-PA complexes is due to the fact that DPA acts as a tridentate ligand and thus forms two stepwise chelates whereas PA acts as a bidentate ligand and forms three stepwise chelates with indium (III).

Acknowledgement

We thank Prof. R. H. Sahasrabudhey, Head of the Department for providing facilities and UGC, New Delhi for the award of a research fellowship to one of us (R.S.).

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