

Thermodynamic Studies of Y(III), La(III), Ce(III) and Sm(III) Complexes of 5-Hydroxy-2-methyl-1,4-naphthalenedione

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The pH-metric and thermodynamic stability have been carried out for yttrium(III), lanthanum(III), cerium(III) and samarium(III) complexes of 5-hydroxy-2-methyl-1,4-naphthalenedione (plumbagin). Three molecules of plumbagin (5-hydroxy-2-methyl-1,4-naphthalenedione) react with these metal ions in solution phase (50% aqueous EtOH, 0.1 M KNO₃ ionic strength) at varied temperatures. The data for yttrium(III), lanthanum(III), cerium(III) and samarium(III) with plumbagin systems reveals a decrease in the value of log pK^H , log k_1 , log k_2 and log k_3 with the increase in temperature; this indicates that the lower temperature is favourable for complexation due to the decrease in the number of collisions and kinetic energy of the molecules and hence their stabilities are lowered.

Key Words: Y(III), La(III), Ce(III), Sm(III), Complexes, 5-Hydroxy-2-methyl-1,4-naphthalenedione, Thermodynamic study.

INTRODUCTION

Literature^{1–22} reveals that the ligand 5-hydroxy-2-methyl-1,4-naphthalenedione (plumbagin) with reference to its chelating properties with $>C=O$ and $-OH$ groups through contributing sites results in the formation of six-membered rings with metal ions. The intra-molecular bonding in this type of ligand culminating into the presence of proton complex in solution was shown by Shapet'ko *et al.*¹ In view of the above, in this paper we report the interaction of 5-hydroxy-2-methyl-1,4-naphthalenedione (plumbagin) (Fig. 1) with yttrium(III), lanthanum(III), cerium(III) and samarium(III), under thermodynamic conditions

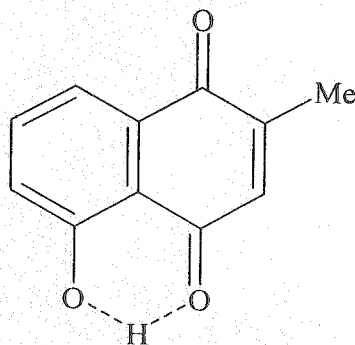


Fig. 1. Structure of the ligand

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and investigations on the interaction of the metal ions in aqueous medium (50% EtOH-water) (v/v) at 0.1 M ionic strength (KNO_3).

EXPERIMENTAL

All chemicals used were procured from E. Merck and Sigma-Aldrich. The pH-metric titrations were carried out with carbonate-free 0.2 M NaOH. The concentration of ligand was always 1×10^{-3} M and that of metal 8×10^{-3} M. An appropriate quantity of KNO_3 , to maintain an ionic strength of 0.1 M, was added. The pH values of the solutions (total vol. 50 mL, medium 50% EtOH-water): (a) 4×10^{-3} M HNO_3 , 1×10^{-1} M KNO_3 , (b) 4×10^{-3} M HNO_3 , 1×10^{-1} M KNO_3 , 1×10^{-3} M ligand and (c) 4×10^{-3} M HNO_3 , 1×10^{-1} M KNO_3 , 1×10^{-3} M ligand, 8×10^{-5} M metal, titrated with 0.2 M NaOH.

Estimations of stability constants of metals and proton complexes were carried out at $28 \pm 0.5^\circ\text{C}$ and $38 \pm 0.5^\circ\text{C}$ employing the Calvin-Bjerrum² pH-titrations techniques. pH was measured on a Metrohm-Herisau E-520 pH-meter having a sensitivity of ± 0.05 and was calibrated before use with suitable buffers. The shapes of the curves (plots of volume of NaOH vs. corresponding pH) were expected. Volume correction due to Van Uitert and Haas³ for the 50% EtOH-water (v/v) system was applied.

RESULTS AND DISCUSSION

The expression of Bjerrum⁴ was used for calculating \bar{n}_H , \bar{n} and pL for proton-ligand formation curves. The free ligand exponent (pL) was calculated following the Bjerrum-Calvin titration techniques⁴.

$$\text{pL} = \log_{10} [(1 + 10^{-\text{pH}} \cdot 10^{\text{pK}^H}) / \Delta\text{NaOH}] \quad (1)$$

where NaOH corresponds to extent of complexation, which can be determined from the separation of metal-ligand curve from the acid curve.

On the progressive addition of 0.2 M NaOH during pH titration a precipitate was obtained in each case. The pH of precipitation in the different systems involving different metals is given in Table-1.

TABLE-1
pH OF PRECIPITATION

Metal	28°C	38°C
Y(III)	5.9	6.1
La(III)	5.8	6.0
Ce(III)	5.6	5.9
Sm(III)	5.7	5.8

The degree of formation (\bar{n}_H) or the proton complex was plotted against the pH-value. The proton-ligand stability $\log \text{pK}^H$ (hydroxyl group), of the ligand was determined by the Bjerrum half integral² and graphical methods⁴. Metal-ligand

stability constants were determined by pointwise and graphical methods⁵. Eqns. 1–4 and 5 due to Bjerrum² for a higher complexity system ($N = 3$) were employed.

$$\log k_1 = pL - \log(1 - \bar{n})/\bar{n} \quad (2)$$

$$\log k_2 = pL - \log(2 - \bar{n})/(\bar{n} - 1) \quad (3)$$

$$\log k_3 = pL - \log(3 - \bar{n})/(\bar{n} - 2) \quad (4)$$

$$\bar{n} \cdot L \cdot k_1/(\bar{n} - 1) + (\bar{n} - 2)L \cdot k_1 \cdot k_2/(\bar{n} - 1) + (\bar{n} - 3)L \cdot k_1 \cdot k_2 \cdot k_3/(\bar{n} - 1) = 0 \quad (5)$$

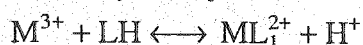
The values of overall change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated with the help of well-known temperature coefficients and Gibbs-Helmholtz equation⁶. Table-2 contains the mean values of protonation constants and thermodynamic functions.

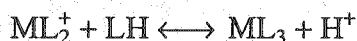
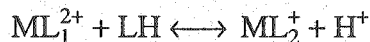
TABLE-2
PROTONATION CONSTANT OF THE LIGAND, STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF THE METAL COMPLEXES

Metal ion	Protonation constants/metal ligands and stability constants	Temperature		$-\Delta G^\circ$ (kJ/mol)		ΔH° (kJ/mol)	ΔS° (kJ/mol)
		28°C	38°C	28°C	38°C	at 38°C	at 38°C
Y ³⁺	log pK_H	11.26	10.80				
	log k_1	9.00	9.27				
	log k_2	8.13	8.50	143.38	154.22	182.81	1.08
	log k_3	7.75	8.13				
	log β_3	24.88	25.90				
La ³⁺	log k_1	8.51	8.95				
	log k_2	7.00	8.35	123.96	138.56	315.44	1.45
	log k_3	6.00	5.97				
	log β_3	21.51	23.27				
Ce ³⁺	log k_1	7.05	8.59				
	log k_2	5.98	7.32	105.98	129.87	612.96	2.39
	log k_3	5.36	5.90				
	log β_3	18.39	21.81				
Sm ³⁺	log k_1	8.95	9.12				
	log k_2	7.19	7.75	128.46	140.70	241.95	1.23
	log k_3	6.15	6.77				
	log β_3	22.29	23.64				

The average number of ligands per metal ion approaches 3 as maximum values for yttrium(III), lanthanum(III), cerium(III) and samarium(III) chelates. The increase in concentration of ligand suggests the formation of three types of complexes with stoichiometry 1 : 1, 1 : 2 and 1 : 3. It is further confirmed by the pH-metric titrations of ligand alone and complexes prepared in the ratios 1 : 1, 1 : 2 and 1 : 3, as per the procedure reported earlier⁷⁻¹¹. The nature of the curves leads to the conclusion that the reaction takes place with the liberation of protons.

Further, pH-metric titrations reveal the release of a proton during complexation in each system; so the reaction may be represented as follows:





where $L = C_{11}H_7O_3$ and $M^{3+} = Y(III), La(III), Ce(III)$ and $Sm(III)$.

The limiting condition was varied with the 1 : 3 metal-plumbagin complex (Fig. 2). The overlapping of curves takes place, which shows that a maximum of three protons is liberated per metal ion in the reaction¹²⁻¹⁴.

The data for yttrium(III), lanthanum(III), cerium(III) samarium(III) with

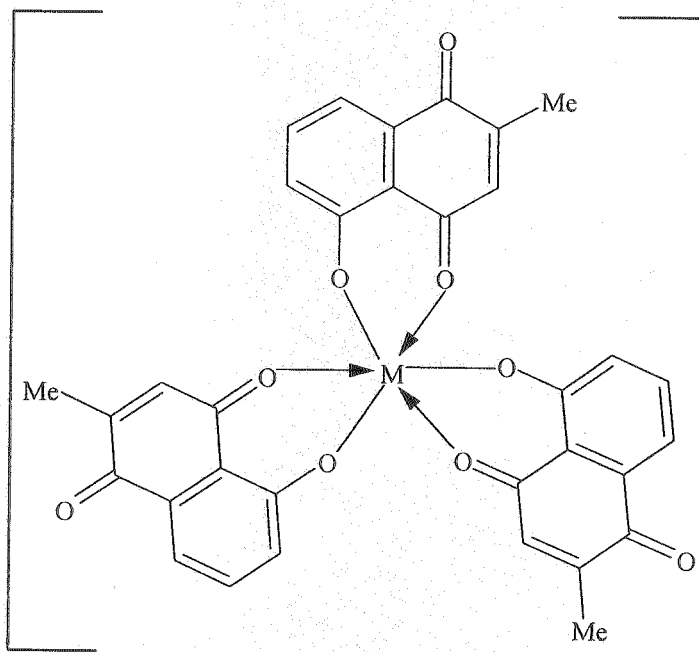


Fig. 2. Metal chelate of plumbagin (5-hydroxy-2-methyl-1,4-naphthalenedione) where $M = Y(III), Sm(III), La(III)$ and $Ce(III)$

plumbagin systems reveal a decrease in the value of $\log pk^H$, $\log k_1$, $\log k_2$ and $\log k_3$ with increase in temperature. This indicates that a lower temperature is favourable for complexation because of the decreased number of collisions with decrease in kinetic energy of the molecules and hence their stabilities are lowered¹⁵⁻¹⁷.

The decrease of the stability of each of the systems ($k_1 > k_2 > k_3$) with each addition of the ligand molecule tallying the expected trend is that the experimental ratio so worked out could not match with the theoretical value(s): $k_2/k_1 = k_3/k_2 = 0.33$ ascertaining that the observation as above is ascribable to the combined effect(s) of statistical and coulombic factors.

The ligand interacts with metal by way of donating an electron pair forming (M—O) bond while —OH group therein acts as a base by the loss of proton in that the anion part of ligand is really participating. The intramolecular bonding in this ligand culminating into the presence of proton-complex in solution was shown by Shapet'ko¹, which found confirmation in the work of Sawhney *et al.*⁷⁻¹⁷ in that the —OH stretching in alcohols usually found in $3650-3500\text{ cm}^{-1}$ range shifted to $3125-3250\text{ cm}^{-1}$ stretch. Secondly, on complexation the bonds 3125 and 1650 cm^{-1} attributable to —OH stretching variation manifesting strong hydrogen bonding in the ligand and the $>C=O$ stretching variation respectively, disappeared and

reduced to 1577 cm^{-1} respectively, showing a secondary bond of a $>\text{C}=\text{O}—\text{M}$ and a primary bond on chelation.

The less negative values of the free energy of formation (ΔG) for all systems indicate the reaction to be a spontaneous process. The enthalpy (ΔH) is positive in all the systems, pointing to the endothermic nature of the reaction and providing explanation for the foregoing inferences. The entropy (ΔS) values are positive in all cases, indicating favourable entropy for formation complexes (Table-2).

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