Stability Constants and Thermodynamic Functions of Some Rare Earth Metal Complexes of O-Hydroxy Dibenzoyl Methane

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Potentiometric studies on the free ligand and the metal complexes of La(III), Pr(III), Nd(III) and Sm(III) with O-hydroxy dibenzoylmethane were carried out in 75% V/V acetone water mixture The stability constants of these complexes formed were computed by Bjerrum—Calvin pH-titration technique, as used by Irving and Rossotti at 27 5° at an ionic strengh of 0 05 M (NaCl)

A review of the literature showed that the stability constants of complexes of lanthanides with O-hydroxy dibenzoyl methane (H_2ODBM) has not been investigated In the present work the metal-ligand stability constants and other thermodynamic functions are reported The complexes of La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} formed with H_2ODBM have been studied potentiometrically by the method of Calvin and Bjerrum[1,2] improved by Irving & Rossotti[3] in 75% V/V acetone water medium The thermodynamic stability constants were determined at 27.5° by conducting experiments at 0.025 M NaCl 0.05 M NaCl and 0.1 M NaCl ionic strength $\Delta G°$, $\Delta H°$ and $\Delta S°$ values were calculated by carrying out experiments at 27 5°, 32 5° and 37 5° respectively.

Experimental :

Materials H_2ODBM was prepared by the procedure described in literature[4]. Rare-earth metal chlorides were prepared from their oxides Small amount of HCl was added in stock solution to check hydrolysis The oxides were estimated gravimetrically by oxalate method Carbondioxide free NaOH was prepared by washing NaOH pallets first for few times by boiling double distilled water and finally dissolving it in double distilled water 1 M NaCl was also prepared in double distilled water for maintaining constant ionic strength

Apparatus .

pH measurements were made using a photovolt pH meter 112—4 with glass and calomel electrodes The thermostatic bath maintained a temperature in the range t $\pm 0.2°$.

Bjerrum-Calvin Titrations ·

For each set of experiments three titrations were carried out. The final volume in every case was 100 ml.

(i) Acid titration   Hydrochloric acid + water + acetone

(ii) Reagent titration   Hydrochloric acid + H_2ODBM + acetone + water.

(iii) Metal titration   Hydrochloric acid + H_2ODBM + metal chloride + acetone + water.

The concentrations of HCl, H_2ODBM and metal chloride in the final volume was 0 01 M, 0 002 M and 0 0005 M respectively. The sodium hydroxide used was ~0 1 M.

An appropriate amount of sodium chloride was added to maintain constant ionic strength.

Results and Discussions

The values of $\bar{n}_A$ at different pH valuse were obtained by expression[3].

$$\bar{n}_A = Y - \frac{(V'' - V')(N + E°)}{(V° + V')T_{CL}} \tag{1}$$

where Y is the number of replaceable hydrogen ions, V' and V'' are the volumes of sodium hydroxide solution for set I and II, N, E°, T_{CL} are the initial concentration of sodium hydroxide, hydrochloric acid and total ligand concentration

The stepwise stability constants were obtained by plotting $\bar{n}$ against pL' where $\bar{n}$ is the average number of ligands attached per metal ion and is given by

$$\bar{n} = \frac{(V''' - V'')(N + E°)}{(V° + V')\bar{n}_A T_{CM}} \tag{2}$$

where V'' is the volume of alkali for third set and T_{CM} is total metal ion concentration pL⁻ the free ligand concentration is given by

$$pL^- = \log \frac{\left\{ \sum_{n=0}^{j} \beta_b^H \left(\frac{1}{\text{antilog } p\text{H}} \right)^n (V° + V''') \right\}}{\{ (T_{CL} - nT_{CM})V° \}} \tag{3}$$

where β_n^H is overall proton ligand stability constant. The pH meter was calibrated for the stoichiometric value of hydrogen ion concentration in acetone water mixture and the pH meter readings were thereafter taken directly for calculation.

Thermodynamic Parameters :

The value of $\triangle G°$ was obtained by expression

$$\triangle G° = -2.303 \, RT \log \beta \tag{4}$$

$\triangle H°$ was determined with the help of an isobar equation

$$\frac{d \ln \beta}{dT} = \frac{\triangle H°}{RT^2} \tag{5}$$

which can also be written as

$$\frac{d \ln \beta}{d(1/T)} = -\frac{\triangle H°}{4.576} \tag{6}$$

The values of $\log \beta$ obtained at different temperatures were plotted as function of $1/T$. The gradient was equated to $-H°/4.576$. The value of $\triangle H°$ thus obtained was used to determine $\triangle S$ according to following equation

$$\triangle H° - \triangle G° = T \triangle S° \tag{7}$$

The values of thermodynamic functions and stability constants are summarised in the following tables.

A graph between pH and volume of alkali required for corresponding pH was plotted. A displacement in the metal titration curve with respect to ligand titration curve indicated that as complexation of metal with ligand took place, the hydrogen ions were liberated. The hydrolysis of metal ion also takes place with the liberation of protons and this process will also give a shift in metal titration curve. Since the hydrolysis of metal ion is only possible at $pH > 8$ and due to the formation of precipitate at $pH \sim 7.5$, the calculations were restricted only up to $pH \sim 7.0$.

The $\bar{n}$ values when plotted against pL^- show two inflexions up to $\bar{n}$ values ~ 3 (Fig. 1). Both indicate the formation of $1:1$; $1:2$ and $1:3$ complexes. The values of pL^- at $n = 0.5$; 1.5 and 2.5 give the stability constant of $1:1, 1:2$ and $1:3$ complexes. The calculations were also carried out by least square method and spreading factor method but they do not show much difference.

The pK value for H_2ODBM was found to be 11.18 at 27.5 and 0.05 M NaCl ionic strength. This suggests H_2ODBM to be a strong chelating ligand and this is confirmed by high values of stability constant as indicated in the table. The value of thermodynamic stability constant was calculated by extrapolating the plot of $\log \beta$ vs ionic strength (μ) to the value $\mu = 0$.

TABLE—1

Metal Ions	Constants	IONIC STRENGTH			
		0.0	0.0125	0.05	0.1
La^{3+}	log k_1	9.48	9.44	8.84	8.40
	log k_2	8.58	8.44	8.12	7.62
	log k_3	7.96	7.78	7.74	7.46
	log $\beta_{cal.}$	26.02	25.66	24.40	23.28
	log β_{exptl}	26.04			
Pr^{3+}	log k_1	9.56	9.54	9.54	8.70
	log k_2	8.66	8.50	8.32	7.92
	log k_3	8.32	8.10	8.02	7.52
	log $\beta_{cal.}$	26.64	26.24	25.46	24.14
	log $\beta_{exptl.}$	26.62			
Nd^{3+}	log k_1	9.58	9.62	9.62	9.16
	log k_2	8.88	8.78	8.48	8.10
	log k_3	8.44	8.30	8.14	7.70
	log $\beta_{cal.}$	26.90	26.70	25.78	24.62
	log $\beta_{exptl.}$	26.98			
Sm^{3+}	log k_1	9.70	9.66	9.42	9.20
	log k_2	8.90	8.88	8.62	8.34
	log k_3	8.66	8.58	8.30	7.98
	log $\beta_{cal.}$	27.28	27.12	26.34	25.52
	log $\beta_{exptl.}$	27.28			

TABLE—2

| Metal Ions	Constants	Temperature			$-\triangle G°$ KJ/MOLE	$\triangle H°$ KJ/MOLE	$\triangle S°$ J/Mole Degree
		27.50	32.50	37.50			
La^{3+}	K1	8.84	8.66	8.44			
	K2	8.12	8.02	7.90			
	K3	7.74	7.64	7.56			
		24.70	24.32	23.90	144.3	-343.3	-651.0
Pr^{3+}	K1	9.12	8.93	8.88			
	K2	8.32	8.29	8.08			
	K3	8.02	7.92	7.80			
		25.46	25.14	24.76	138.0	-329.9	-631.8
Nd^{3+}	K1	9.16	9.00	8.96			
	K2	8.48	8.36	8.22			
	K3	8.14	8.04	7.88			
		25.78	25.40	25.06	137.1	-217.5	-626.6
Sm^{3+}	K1	9.42	9.22	9.18			
	K2	8.62	8.56	8.38			
	K3	8.30	8.06	7.96			
		26.34	25.84	25.52	136.8	-326.8	-622.0
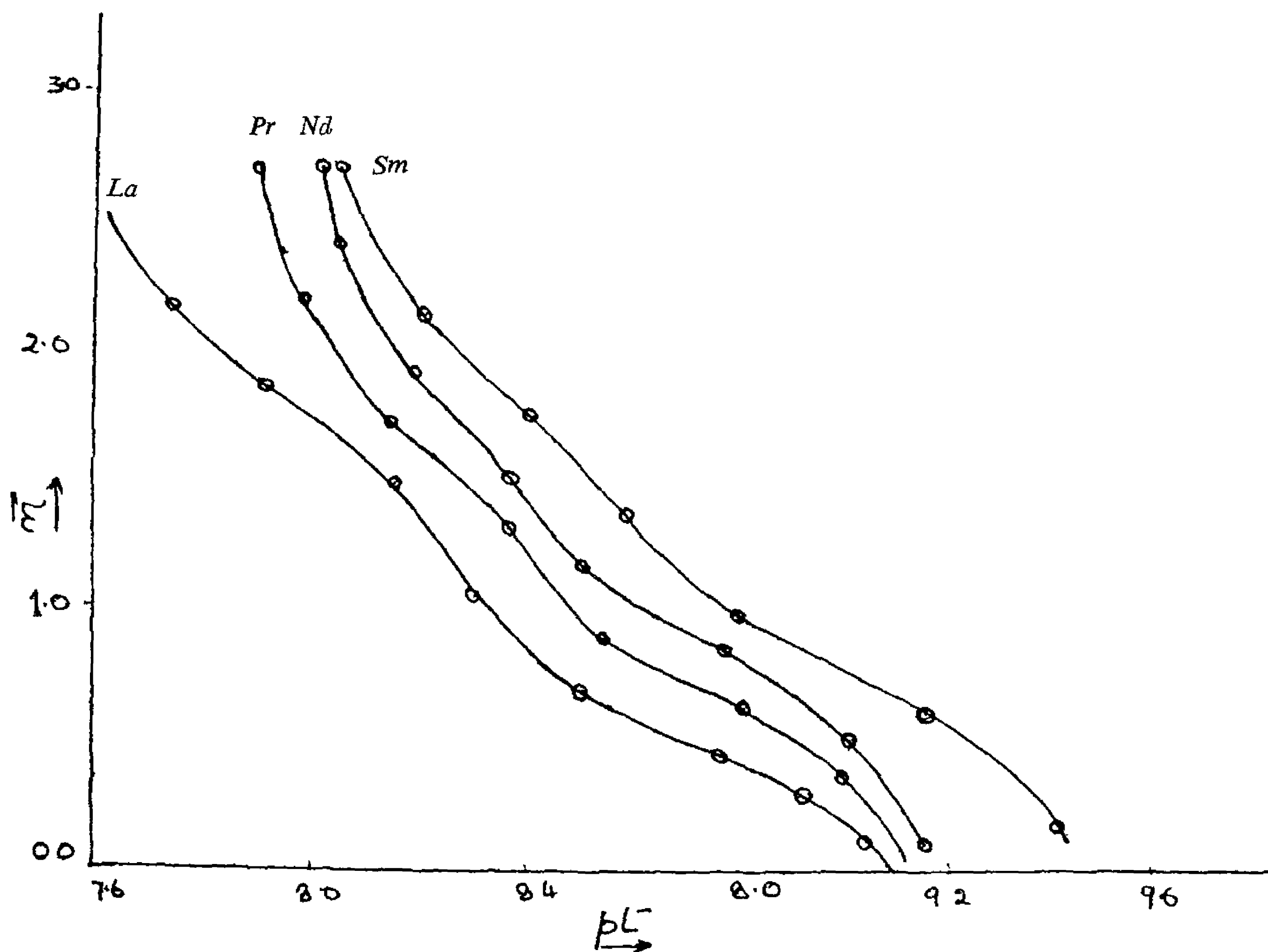
Fig. 1. Ligand O-Hydroxy Debenzoylmethane
Temp.--32 5°
Ionic Strength 0.05M NaCl

Reference

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