# Electrometric Studies of Some Rare Earth Metal Complexes with Phloroacetophenone

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The stability constant (log k) of La(III), Ce(III), Pr(III), Nd(III) and Gd(III) with phloracetophenone (2, 4, 6-trihydroxy-acetophenone) have been evaluated by Irving-Rossotti technique at $25 \pm 0.1°$ in 50% dixoane-$H_2O$ system at an ionic strength of $0.1M$ $NaClO_4$. The stoichiometric ratio of metal-ligand (1 : 1) have been studied by $p$H-metric titration method. The order of stability constants follow the well established order, i.e.,—

La(III)<Ce(III)$\leq$Pr(III)<Nd(III)$\leq$Gd(III)

The values of stability constant (log k) and change in free energy ($\Delta$G) in K cal/mole for La(III), Ce(III), Pr(III), Nd(III) and Gd(III) are 3.19, 3.39, 3.31, 3.71, 3.69 and −4.36, −4.61, −4.51, −5.06, −5.04 respectively.

COMPLEXES of transition metal ions with several o-hydroxyacetophenones have been investigated by different group of workers. The complexes of phloroacetophenone (2, 4, 6-trihydroxyacetophenone, referred to herein as (PAP) with transition metals have also been studied. Recently the author[1] studied the interaction of PAP with ZrO(II) and Th(IV) by potentiometric method. The literature survey reveals that the study of interaction of inner transition metals, i.e., rare-earth metals •of lanthanides with such ketones is not so common. Therefore, in this paper the interaction of rare-earth metals La(III), Ce(III), Pr(III), Nd(III) and Gd(III) with PAP has been taken.

## Experimental

The PAP was prepared by the method as described in earlier publication[1,2]. Dioxane was dried with Na and distilled twice[3]. Solution of rare-earth metal perchlorates were prepared in conductivity water by dissolving rare earth metal oxides in the calculated quantity of $HClO_4$ and the metal content were gravimetrically estimated[4,5]. All the chemicals used were AnalR(B. D. H. or equivalent). The following sets were prepared for $p$H-titrations in 50% dioxane-$H_2O$(v/v) medium.

(i) 5 ml of $0.5M$ $HClO_4$+4.75 ml of $1M$ $NaClO_4$+15.25 ml of $H_2O$. (ii) 5 ml of
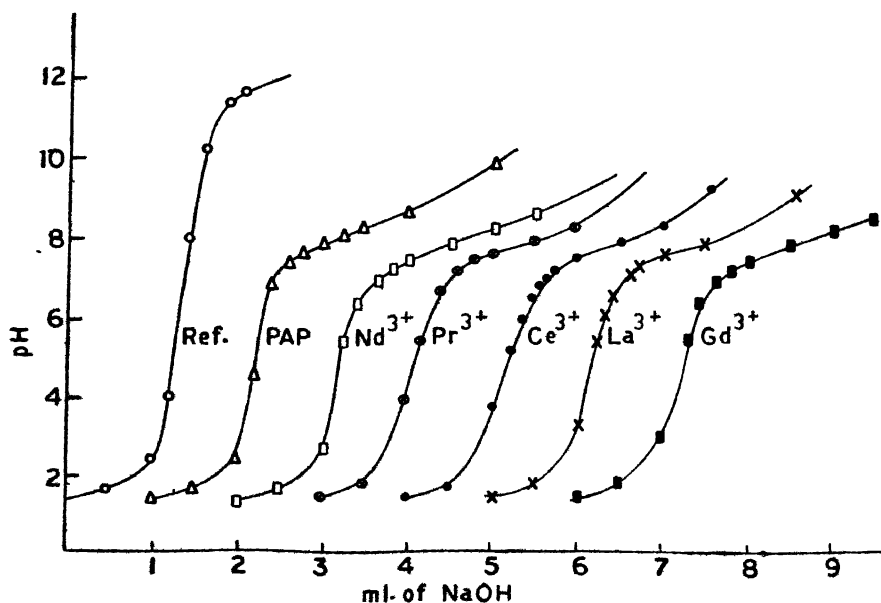


Fig. 1 $p$H-metric titrations of PAP in absence and presence of metal ions.

0.5 $M$ HClO$_4$+4.25 ml of 1$M$ NaClO$_4$ +10 ml of 0.5$M$ PAP+5.75 ml of H$_2$O. (iii) 5 ml of 0.5$M$ HClO$_4$+3.95 of 1$M$ NaClO$_4$+10 ml of 0.5$M$ PAP+5 ml of 0.01$M$ metal perchlorate+1.05 ml of H$_2$O.

In all the $p$H-titrations the ionic strength (0.1$M$ NaClO$_4$). Volume (25 ml), temperature (25 ±0.1°) were kept constant. Necessary corrections were made for $p$H-measurements due to change of medium, i.e., 50% dioxane-H$_2$O medium[6]. $p$H measurements were carried out on radiometer $p$H-meter (PHM-4) with glass-calomel electrodes. Calomel electrode was connected to the titration vessel by means of salt bridge saturated with KCl.

## Results and Discussion

The proton-ligand stability constant (log P$^K$H) and dissociation constant of PAP were already reported by the author[1] and they are 8.608 and 2.455×10$^{-9}$ respectively. $p$H-readings for all sets were plotted against the moles of NaOH (Fig. 1). As most of the $p$H-metric curves for these metals show only a little difference between $p$H-range 5.75 to 7.75, curves for all the sets in the Fig. 1, are plotted to such a manner so that the curves have a common difference between them. The metal-ligand stability constant of rare-earth metals with PAP were calculated by Bjerrum's method[7,8,9] as adopted by Irving-Rossotti[10]. The formation curves of metal-PAP complexes are shown in the Fig. 2.
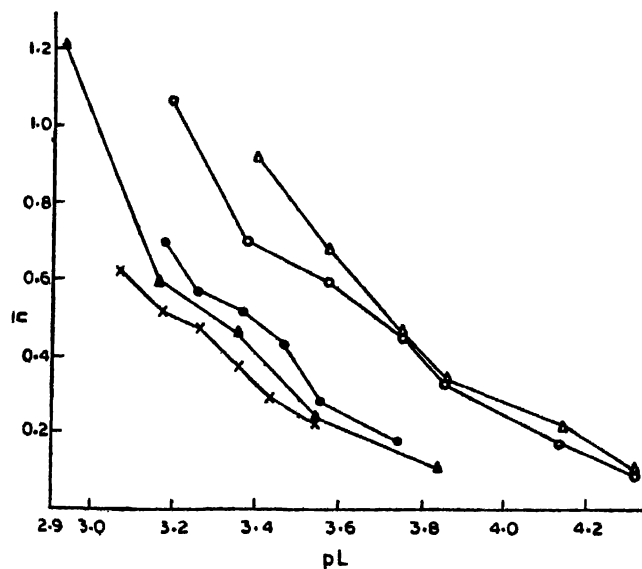


Fig. 2. Formation curves of Metal-PAP Complexes.

× ×—La (III)
● ●—Ca (III)
△ △—Pr (III)
⊓⊓—Na (III)
○○—Gd (III)

The stability constant of the complexes and change in free energy at $\bar{n}$=0.5 for 1 : 1 metal-ligand ratio at 25 ±0.1° are given in the table. In most of the cases the complexation occurs in the $p$H-range 6.0-7.75, after that hydroxide formation takes place.

The ratio of metal-ligand interaction were also determined by $p$H-metric titrations. The limits of

### TABLE

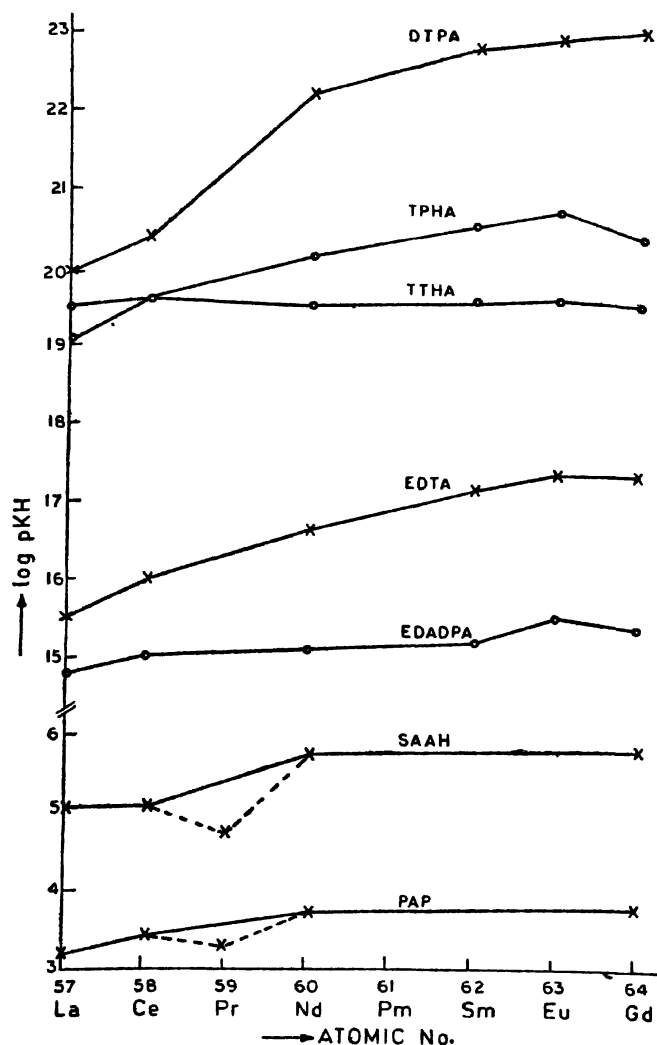| Metal | Atomic No. | Electronic configuration | M$^{s+}$ radii | Stability constant (log k) | Change in free energy (ΔG) in K cal/mole |
|---|---|---|---|---|---|
| La(III) | 57 | 4 f$^0$ | 1.06 | 8.19 | −4.36 |
| Ce(III) | 58 | 4 f$^1$ | 1.03 | 8.39 | −4.61 |
| Pr(III) | 59 | 4 f$^2$ | 1.01 | 8.31 | −4.51 |
| Nd(III) | 60 | 4 f$^3$ | 1.01 | 8.71 | −5.05 |
| Gd III) | 64 | 4 f$^7$ | 0.94 | 8.69 | −5.04 |



Fig. 3. Plot of atomic number with stability constant (log k) of the following ligands :

(I) Phloracetophenone (PAP)

(II) Salicyl aldehyde-alanine (d 1) Schiff's Base (SAAH).

(III) Ethylene Diamine Tetra Acetic Acid (EDTA).

(IV) Triethylene Tetraamine Hexacetic Acid (TTHA).

(V) Tetra ethylene Pentamine Hepta Acetic Acid (TPHA).

(VI) Ethylene Diamine Diacetic Acid Dipropionic Acid (EDADPA).

(VII) Diethylene Triamine Penta Acetic Acid (DTPA)

error in the calculation of log $k$ and change in free energy ($\Delta$G) are 0±0.05 and 0±0.07 respectively.

On going through the values as given in the table, stability constant (log $k$) for La(III), Ce(III), Pr(III), Nd(III) and Gd(III) have an appreciable, difference which cannot be attributed due to experimental and/or calculation errors. Thus the stability constant (log $k$) follow the following order :

La(III)<Ce(III)≤Pr(III)<Nd(III)≤Gd(III)
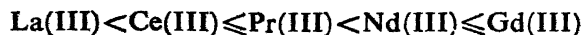
The lanthanides have very close chemistry and difference in the values of stability constants, if any, is mainly due to *lanthanide contraction*. The similar type of behaviour for lanthanide complexes with several other complexing agents were also observed by the author[11] and different other group of workers[12,13 14]. In Fig. 3 various curves show the stability constants (log $k$) of aforesaid rare-earth metals with different ligands. In the curves deviation, if any, are shown by the dotted portion.

## Acknowledgement

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