CHAPTER THREE

BINARY COMPLEXES OF CO(III), Pr(III) AND Mn(III)
WITH THE DERIVATIVES OF ACETIC ACID
AND BENZOIC ACID
LIST OF PUBLICATIONS ON THE PRESENT STUDY

1. Complexes of Praseodymium(III) with glycine, iminodiacetic acid and nitrilotriacetic acid, a polarographic study.

2. Complexes of Neodymium(III) with glycine, iminodiacetic acid and nitrilotriacetic acid, a polarographic study.

3. Stepwise stability constants of Cerium(III) with glycine, iminodiacetic acid and nitrilotriacetic acid, a polarographic study.


5. Study of complexes of Pr(III) with benzoic acid, protocatechuic acid and salicylic acid on a DME.

6. Complexes of Cerium(III) with benzoic acid, protocatechuic acid and salicylic acid: a polarographic study.
Our knowledge of the world in which we live and the matter with which we deal is steadily growing. Each day brings new facts and details. Every field of knowledge splits into more and more levels of individual investigations. The scope of the chemistry of co-ordination is so wide that it is almost a meeting place of inorganic, organic, physical, analytical and theoretical chemistry.

Co-ordination compounds are of particular importance in the chemistry of transition and inner transition elements, where tendency of complexation is developed due to the availability of incompletely filled 'd' and 'f' orbitals. The lanthanides, fourteen in number, commonly known as 'Rare earths' and lanthanones (from atomic number 58 to 71), have incompletely filled 'f' and 'g' orbitals and are placed together as a bunch of elements, in the third group of the periodic table. The trivalency among these elements can be explained with 5d¹, 6s², 6p⁰ configuration in ultimate and penultimate orbits²(a), the incoming electron comes in the '4f' orbital and hence they are also known as '4f' block elements. All these elements generally show hexa co-ordination number with d²sp³ hybridisation, forming octahedral geometry of the complex.
SURVEY OF LITERATURE

Lanthanides are known to form well crystallised double nitrates with nitrates of ammonia and some bivalent metals. A few sulphates, carbonates and chlorides are also known to be formed.²(b)

Rare earth chelates with aminopolycarboxylic acids have been investigated from the point of view of their separation³. Some citrate complexes of rare earths have been studied.⁴

Complexes of Pr, Sm, Gd and Dy chlorides with diethyl oxalate, malonate, succinate and those of La and Nd chlorides with diethyl adipate, malonate and phthalate have been prepared.⁵

Koreman and Sokolov⁶ have studied the stability constants of malonate and succinate complexes of rare earths, while Kastramiskhim and Rastvecov⁷ have calculated the stability constants of rare earths complexes with organic ligands.

Kresse⁸ studied the complexes of rare earths with organic ligands, co-ordinated through nitrogen and oxygen atoms.

Methylamine complexes of rare earths of the type $\text{McCl}_3.n\text{Me}_2\text{H}_2$ where $n = 2$ to 5 (decomposition
temperature 15° - 20.5°C) have been reported by Alexander et al.9

A preliminary spectrophotometric study of Pr and Nd complexes in fused salt was done by Crunn10 and it was noted that fused salt absorption spectra were broader and showed displacement towards longer wavelength. Studies of complex formation of Pr(III) with unsaturated amines were undertaken spectrophotometrically by Avakyan and Spyan11.

Spectrophotometric study of carbonate complexes of rare earths was carried out by Polusктove and Kononeko12.

The complexes of Pr and Nd with EDTA and NTA have been studied by Vagma and Yu-liang yung13.

Stability constants of complexes of La, Ce, Pr and Nd with aspartic, Malic, thiomalic, anthranilic, glycolic, salicylic, thioglycolic acids were determined at 30°C potentiometrically14.

Serchenka, Kyzretova and Khomenko have synthesised complex compounds of rare earths with organic molecules, such as dibenzoyl methane, benzoyl acetone, acetyl acetone, derivatives of salicylic aldehyde, salicylic acid, α-oxy quinoline and α-substituted pyridine compounds and studied them spectrophotometrically15.
Stability constants of the lighter rare earths complexes with glutamic acid were determined by pH metric and potentiometric techniques\textsuperscript{16}. Agrawal and co-workers have also studied thermodynamic parameters for the same\textsuperscript{17,18}.

Bhatnagar et.al studied the ternary complexes of rare earths with citraconic, phthalic, malonic, meleic and 8-hydroxy quinolines by pH metric technique\textsuperscript{19}.

Stability constants and thermodynamic parameters of aspartic acid with rare earths have been determined potentiometrically\textsuperscript{23-22}, where as solid complexes were prepared by Farooq et.al\textsuperscript{23}.

Mixed ligand complexes of some rare earths with EDTA and some dicarboxylic acids were studied pH metrically\textsuperscript{24}.

Azide complexes of some rare earths have also been prepared\textsuperscript{25,26}.

Stability constants of some rare earths complexes with mendallic acid have been reported\textsuperscript{27}.

Solid complexes of some rare earths with hydrazine were also prepared and stability constants were determined pH metrically\textsuperscript{28}. 
Stability constants and thermodynamic parameters of some rare earths with tyrosine were also studied potentiometrically\textsuperscript{29,30}.

Polarographic determination of stability constant of Eu(III)-complexes with acrylic acid and erucic acid have been reported by Rao and Singh\textsuperscript{31}.

Gluconate complexes of Sm(III), Gd(III), Dy(III) and Ho(III) have been reported by potentiometric technique\textsuperscript{32}.

Saxena and Saxena have reported the stability constant of some rare earth complexes with N-butylthio glycolate potentiometrically in 40\% ethanol\textsuperscript{33}.

Ternary complexes of Nd(III) by taking picolinic acid, thiglycolic acid and thi di-propionic acid as primary ligand and some dicarboxylic acid as secondary ligands have been reported by Shelke and Jahagirdar\textsuperscript{34}.

Thermodynamic study of complexation of some rare earths with 3-hydroxy naphthalene-2 carboxylic acid has been reported by Sandhu and Kumaria potentiometrically\textsuperscript{35}.

Similarly gluconate complexes\textsuperscript{36}, isoxazoles\textsuperscript{37} have been also reported. Some ligands e.g.
phloroglucinol$^{38}$, dimethylacetamide$^{39}$ have also been used for complexation with rare earths.

Makadeo and coworkers have reported some new rare earths complexes with substituted naphthalene derivatives and schiff's bases$^{40-45}$.

Patil and Darshane have reported electrical properties of lanthanide-pyroclore$^{46}$.

Lanthanide complexes with N=O donor ligands have been studied by Mishra and Singh$^{47}$.

Dissociation constant and stability constants of trivalent La, Ce, Pr, Nd and Sm with glycy1-D-L-leucine have also been reported$^{48}$.

Potentiometric study of complex formation of some trivalent rare earths with 2-hydroxy-1 naphthalidene-2-imino pyridine have been reported by Sengupta and Bera$^{49}$.

Rana and Tandon have reported some mixed chelates of trivalent La, Pr and Nd with -N-hydroxy ethylenediamine N, N', N'' trisacetic acid as primary ligand and mercapto acids as secondary ligands potentiometrically$^{50}$.

Bhuyan and Dubey have reported the chelation of some lanthanones with substituted naphthaline, tyren
and catechol $^{51-53}$.

Munshi and coworkers have also reported some binary and ternary complexes of lanthanons $^{54-56}$. Recently, binary and ternary complexes of some lanthanons with EDTA as primary ligand and tartrazine as secondary ligand have been reported potentiometrically $^{57}$. Some new protonated ternary complexes with DTPA, $C_y$DTA and keto-glutaric acid have been reported by potentiometric technique $^{58}$. Potentiometric study of trivalent Pr, Nd, Sm, Gd and Dy complexes with substituted naphthaquinone have been done by Rao and Reddy $^{59}$. Spectrophotometric studies of lanthanide complexes with PAN in water ethanol media have been made by Rao and Satyanarayan $^{60}$. Pitre et al. have reported some complexes of rare earths with dyes and aminopoly-carboxylic acids amperometrically and polarographically $^{61-65}$.

However, a survey of literature reveals that a polarographic study of complex formation of trivalent Ce, Pr, and Nd with glycine, iminodiacetic acid, nitrilotriacetic acid (derivatives of acetic acid), benzoic acid, protocatechuic acid and salicylic acid (derivatives of benzoic acid) abbreviated as Gly, IDA, NTA, BA, PCA and SA respectively, have not been made.

The present chapter deals with the composition and stability constants of binary complexes formed of
Ce(III), Pr(III) and Nd(III) with the above mentioned ligands by Lingane and Deford-Hume's treatment of the observed polarographic data.

**EXPERIMENTAL**

All the chemicals used were of AnalyR/BDH grade. Stock solutions of glycine, IDA and NTA (0.1 mol dm⁻³) were prepared by direct weighing the requisite quantity of the chemicals in doubly distilled water, where as stock solutions of each of the organic aromatic acid was prepared by heating a mixture of requisite quantity of the chemical with gram equivalent quantity of sodium carbonate in distilled water and finally the residue was extracted and diluted upto the mark by doubly distilled water. The solutions of metals, potassium chloride and gelatin were prepared as mentioned in Chapter II, page 47.

In each case a preliminary experimental set was prepared by keeping overall concentrations of potassium chloride, gelatin and metal ion fixed at 1.0 mol dm⁻³, 0.01x and 1 m mol dm⁻³ respectively. In other sets in addition to the above supporting electrolyte, maximum suppressor and metal ion, the concentration of each of the ligand was varied.
Polarograms were recorded on a CIC (Barela, India) automatic pen recording polarograph. Pure nitrogen gas was passed through the test solutions for deaeration. The capillary characteristics of the DME were $m = 2.37 \text{ mg} \cdot \text{s}^{-1}$, $t = 3.0 \text{ s}$ at 35 cm effective height of the mercury head. $(m^{2/3} t^{1/6} = 2.136 \text{ mg}^{2/3} \text{ s}^{-1/2})$. The pH of the test solutions was fixed by necessary addition of sodium hydroxide/hydrochloric acid solutions. For pH measurements an Elico digital pH meter (model LL-120) was used. All the observations were made at room temperature (24 ± 2)°C.

**Discussion of the Results**

Each of the three metals Ce(III), Pr(III) and Nd(III) give well defined reversible, three electron reduction waves in 1.0 mol dm$^{-3}$ potassium chloride, in presence of 0.01% gelatin in the pH range 2.2 ± 0.02 to 3.2 ± 0.02. The reduction of these metals and their complexes with various ligands, mentioned above is found to be diffusion controlled as revealed from the linear plots of $I_d$ vs $E_{d}$, passing through the origin. The plots of log $1/I_d$ vs $E_{d}$ for each polarogram is linear with a slope of 20 ± 1 mV, indicating the reversibility of the electrode process involving three electron reduction in each case.
Effect of Ligand Concentration

On gradual increase of the ligand concentration, the half wave potential of the metal ion is shifted to more negative value in each case. The diffusion current is also decreased with increasing ligand concentration, thereby showing the complex formation with various ligands understudy, with all the three rare earths.

Stoichiometry of the Complexes

To study the composition and stability constants of binary complexes, plots of $\Delta E_{1/2}$ (shift in the half wave potential $\Delta E_{1/2} = (E_{1/2})_e - (E_{1/2})_i$) against $\log C_X$ (logarithm of the concentration of the ligand) are drawn. The plots are either linear or segmented lines showing thereby the formation of single or plural complex species, respectively.

For evaluating the stability constants of the single complex and the number of ligands 'p' attached with the central metal ion, the method of Lingane is applied\textsuperscript{72}, which involves the following equations:

$$\frac{\Delta E_{1/2}}{\Delta \log C_X} = -p \quad \frac{0.05915}{n} \quad \ldots \ldots \ldots \ldots \ldots (1)$$
\[ \Delta E_{1/2} = \frac{0.03915}{n} \log K_c - \frac{0.03915}{n} p \log C_x \ldots (2) \]

Where the various symbols have their usual meaning.

For evaluating the stability constants of the consecutive complexes, the method of Deford and Hume\(^73\) is applied, in which a shift in \(E_{1/2}\) is noted and then various \(F_{0}(x)\) functions are calculated for each value of \([X]\) by the following equation:

\[ F_{0}(X) = \text{antilog} \left[ \frac{0.03433 - nF}{n} \Delta E_{1/2} + \log \frac{I}{I_c} \right] \ldots (3) \]

In order to determine \(\beta_1, \beta_2, \ldots, \beta_n\), the graphical method of extrapolation as devised by Ledon\(^74\) is applied.

\[ \text{and} \]

1. Complexes of \(Ce(III), Pr(III), \text{and } Am(III)\)

With the Derivatives of Acetic Acid.

Amine acids have been extensively used for complex formation with various metals\(^75-79\). Among the amine acids, the chelating tendency of the derivatives of acetic acid is noteworthy. It is interesting to note that glycine, LXA and NLA have a remarkable similarity, due to the presence of amino as well as acetic acid groups, as exhibited by their
Out of these only NTA forms 1:1 complexes with most of the metals, whereas glycine and IDA forms 1:1, 1:2 and 1:3 complexes with various metals.

a. Glycine Complexes.

Glycine is a bidentate ligand and contains one carboxylic acid group and one nitrogen atom for coordination. Monk has studied lanthanum-glycine system polarographically and reported the formation of 1:1 and 1:2 complexes. Keefer has reported 1:1 and 1:2 complexes of Cu(II) with glycine. Evans and Monk have studied 1:1 and 1:2 complexes of Co(II) with glycine. Kapoor and Jaikishan have reported
Plot of $-E_{1/2}$ vs $\log$ [Glycine] for

(A) Ce(III) - Glycine system,
(B) Pr(III) - Glycine system and
(C) Nd(III) - Glycine system.
In(III)-glycine complexes polarographically.

In the present study it is observed that Ce(III) forms 1:1 and 1:2 successive complexes where as Pr(III) and Nd(III) form 1:1 complex with glycine as revealed from the smooth curve and staright line plots of $E_{1/2}$ vs log $C_x$ (logarithm of the concentration of glycine) [Fig. 3.1]. The polarographic data and functions of Ce(III)-glycine system has been tabulated in table 3.1 and that of Pr(III) and Nd(III)-glycine systems in table 3.2.

The stoichiometry of the complexes with their stability constants is as under:

1. $[\text{Ce-(Gly)}]^2^+$ 1:1  $\log \beta_1 = 3.69$
2. $[\text{Ce-(Gly)}]^+ 2$ 1:2  $\log \beta_2 = 6.00$
3. $[\text{Pr-(Gly)}]^2^+$ 1:1  $\log \beta_1 = 3.50$
4. $[\text{Nd-(Gly)}]^2^+$ 1:1  $\log \beta_1 = 4.00$

Ce(III)-glycine system has been studied at pH 3.0 ± 0.02, where as Pr(III)-glycine and Nd(III)-glycine systems have been studied at pH 2.75 ± 0.02.

b. **IDA Complexes.**

IDA is a tridentate ligand containing one nitrogen atom and two carboxylic acid groups for metal-ligand co-ordination. Schwarzenbach et.al have
Plot of $-E_{1/2}$ vs $-\log \text{[IDA]}$ for

(A) Ce(III) - IDA system,
(B) Pr(III) - IDA system and
(C) Nd(III) - IDA system.
studied divalent metal complexes with IDA potentiometrically and conductometrically. Chaberck and Martell have also studied metal complexes with IDA. In(III)-IDA complexes have been reported in aqueous and partially non-aqueous media.

In the present study Ce(III) forms 1:1 and 1:2 complexes with IDA, while Pr(III) and Nd(III) both form 1:1 complexes with IDA, which is clear from the smooth curve and straight line plots of $E_{1/2}$ against log $c_x$ (logarithm of the concentration of IDA) [Fig. 3.2]. The polarographic data and various functions of Ce(III)-IDA system have been listed in table 3.3 and that of Pr(III)-IDA and Nd(III)-IDA systems in table 3.4.

The stoichiometry of the complexes and their stability constants is as under:

1. $\text{[Ce(IDA)]}^+$ 1:1 $\log \beta_1 = 3.99$
2. $\text{[Ce(IDA)O]}^-$ 1:2 $\log \beta_2 = 6.27$
3. $\text{[Pr(IDA)]}^+$ 1:1 $\log \beta_1 = 3.80$
4. $\text{[Nd(IDA)]}^+$ 1:1 $\log \beta_1 = 4.36$

Like glycine system, Ce(III)-IDA system has been studied at pH 3.0 ± 0.02, whereas Pr(III)-IDA and Nd(III)-IDA systems have been studied at pH 2.75 ± 0.02.
Plot of $-E_{1/2}$ vs $-\log [\text{NTA}]$ for

(A) Ce(III) - NTA system,
(B) Pr(III) - NTA system and
(C) Nd(III) - NTA system.
NIA Complexes.

NIA is a quadridentate ligand with three carboxylic acid groups and one nitrogen as co-ordination group for metal chelate formation. Marsh has reported rare earths with NIA$^2$. Shedov et al. have studied binary metal complexes with NIA$^8$. Munshi et al. have used it as a strong primary ligand in ternary systems$^9$.

In the present study the plots of $E_{1/2}$ against log $C_N$ (logarithm of the concentration of NIA) revealed linear lines, suggesting the formation of 1:1 single complex species with all the three metals, under study [Fig. 3.3]. The study of Ce(III)-NIA system has been made at pH 3.05 ± 0.02, while pH 2.75 ± 0.02 was used for the study of Pr(III)-NIA and Nd(III)-NIA systems. All the polarographic data for these systems have been given in table 3.5.

The stoichiometry and stability constants of the complexes are as under:

1. [Ce(NTA)] 1:1 log $\beta_1 = 5.90$
2. [Pr(NTA)] 1:1 log $\beta_1 = 4.20$
3. [Nd(NTA)] 1:1 log $\beta_1 = 4.78$
Inference

A perusal of Fig 3.1 to 3.3 and Table 3.1 to 3.5 and above paras show that Ce(III) forms 1:1 and 1:2 step wise complexes with glycine and IDA respectively, whereas 1:1 complex formation is observed with NTA. On the other hand Pr(III) and Ni(III) both form 2:1:1 complex with all the three ligands as mentioned above.

However, literature records higher values for the stability constants of above studied chelates. The difference in the stability constants may be attributed to the lower pH value of the experimental sets. The various ligands in the above studied chelates, follow the order for the stability constants:

Glycine < IDA < NTA.

The increased value of metal ligand stability constants in the above order, may be explained on the basis of the presence of two acetic acid groups in IDA and three acetic acid groups in NTA, which renders these ligands a good deal more reactive towards the generality of the cations, than glycine, as a result of which increased liganding ability is observed from glycine to NTA.
II. Complexes of Ce(III), Pr(III) and Nd(III) with Benzoic acid and its Hydroxy Derivatives.

Benzoic acid and its substituted hydroxy derivatives have been extensively used for complex formation with various metals, involving various electroanalytical techniques\textsuperscript{92-96}. In the present study benzoic acid (BA), protocatechuic acid (3:4 dihydroxy benzoic acid) (PCA) and salicylic acid (SA) have been used as complexing agents with Ce(III), Pr(III) and Nd(III) respectively on a DME. Out of these BA forms 1:1 complex with various metals, whereas 1:1, 1:2 and 1:3 complexes are formed by protocatechuic acid and salicylic acid respectively.

a. Benzoic acid Complexes

Benzoic acid is the first acid of the aromatic series. There is a benzene ring and one carboxylic acid group is attached to one of its carbon atoms. It has been used as a complexing agent. Leden reported the formation of silver benzoate complex\textsuperscript{97}. Jain et.al. have reported the polarographic study of Tl(I) and Pb(II) complexes with benzoic acid\textsuperscript{98}.
[FIG. 3.4]

- $E_{1/2}$ vs. SCE

- $1.88$ (A)
- $1.86$
- $1.84$
- $1.82$
- $1.80$

- $-\log [BA]$

**Plot of $-E_{1/2}$ vs. $-\log [BA]$ for**

(A) Ce(III) - BA system,
(B) Pr(III) - BA system and
(C) Nd(III) - BA system.
In the present study it is observed that Ce(III), Pr(III) and Nd(III) form 1:1 complex with BA as revealed from the straight line plots of $E_{1/2}$ vs $\log C_x$ (logarithm of the concentration of benzoic acid) [Fig. 3.4]. The polarographic data have been listed in table 3.6. The composition and stability constants of various complexes are as under:

1. $[\text{Ce(BA)}]^{2+}$ 1:1 $\log \beta_1 = 4.10$
2. $[\text{Pr(BA)}]^{2+}$ 1:1 $\log \beta_1 = 3.40$
3. $[\text{Nd(BA)}]^{2+}$ 1:1 $\log \beta_1 = 3.45$

The Ce(III)-BA system has been studied at pH 3.00 ± 0.02, whereas Pr(III)-BA and Nd(III)-BA systems have been studied at pH 2.40 ± 0.02 respectively.

b. Protocatechuic acid System

Protocatechuic acid (3,4 dihydroxy benzoic acid) has also been used as a complexing agent. In the present study the straight line plots of $E_{1/2}$ vs $\log C_x$ (logarithm of the concentration of PCA) are observed [Fig. 3.5], thereby showing the formation of single complex species with all the three metals under study. They all form 1:2 complex with PCA.

The polarographic data have been listed in table 3.7. The composition and stability constants of
Plot of $E_{1/2}$ vs log [PCA] for
(A) Ce(III) - PCA system,
(B) Pr(III) - PCA system and
(C) Nd(III) - PCA system.
various complexes are as under:

1. $[\text{Ce(PCA)}_2]^{3-}$ 1:2 $\log \beta_2 = 6.28$
2. $[\text{Pr(PCA)}_2]^{3-}$ 1:2 $\log \beta_2 = 7.14$
3. $[\text{Nd(PCA)}_2]^{3-}$ 1:2 $\log \beta_2 = 7.54$

Ce(III)-PCA system has been studied at pH 3.00 ± 0.02, where as Pr(III)-PCA and Nd(III)-PCA systems have been studied at pH 2.43 ± 0.02.

c. Salicylic acid Complexes.

Salicylic acid is known to form complexes with several metal ions. Babko has reported 1:1, 1:2 and 1:3 complexes of Fe(III) with SA, while Foley and Anderson have reported Al(III)-SA system. Jain et al. have reported Pb(II), Ti(II) complexes with SA polarographically.

In the present study it is observed that Ce(III) forms 1:1 and 1:2 successive complexes with SA, whereas each Pr(III) and Nd(III) forms 1:2 complex with SA, which is revealed from the segmented and straight line plots of $E_{1/2}$ vs $\log C_x$ (logarithm of the concentration) [Fig. 3.6]. The polarographic data and various functions for Ce(III)-SA system is tabulated in table 3.8, whereas polarographic data for Pr(III)-SA and Nd(III)-SA systems have been listed in table 3.9.
Plot of $-E_{1/2}$ vs $-\log [SA]$ for

(A) Ce(III) - SA system,
(B) Pr(III) - SA system and
(C) Nd(III) - SA system.
The composition and stability constants of various complexes are as under:

<table>
<thead>
<tr>
<th></th>
<th>Lingane Method</th>
<th>Deford Hume's Method</th>
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<tbody>
<tr>
<td>1. ([\text{Ce(SA)}])^+</td>
<td>1:1</td>
<td>(\log \beta_1 = 3.60)</td>
</tr>
<tr>
<td>2. ([\text{Ce(SA)}_2])^-</td>
<td>1:2</td>
<td>(\log \beta_2 = 7.20)</td>
</tr>
<tr>
<td>3. ([\text{Pr(SA)}_2])^-</td>
<td>1:2</td>
<td>(\log \beta_2 = 7.48)</td>
</tr>
<tr>
<td>4. ([\text{Nd(SA)}_2])^-</td>
<td>1:2</td>
<td>(\log \beta_2 = 7.70)</td>
</tr>
</tbody>
</table>

The Ce(III)-SA system has been studied at pH 3.30 \(\pm\) 0.02, whereas Pr(III)-SA and Nd(III)-SA systems have been studied at pH 2.40 \(\pm\) 0.02.

**Inference**

Thus it is clear that all the three metals form 1:1 simple co-ordination compounds with benzoic acid, whereas PCA and SA form chelates. Only Ce(III) forms 1:1 and 1:2 successive complexes with SA, while PCA forms 1:2 complex with all the three metals under study. Various ligands in the above studied complexes follow the order for the stability constants:

\[ BA < PCA < SA. \]

Which may be explained on a simple argument that BA forms a simple co-ordination compounds with all
the metals under study, while PCA and SA form chelates. The difference in the stability constants of PCA and SA complexes can be explained on the presumption that the chelating groups (hydroxyl and carboxylic acid groups) in SA are in O-position, whereas in PCA two hydroxyl groups are in m- and p-positions with respect to carboxylic acid group. This renders SA to behave as a stronger chelating agent than PCA as also observed by Bhattacharya et al. 99
### TABLE 3.1

**Ce (III) - GLYINE SYSTEM**

**Concentration of the Metal ion** = 0.5 mm

**Concentration of K.1** = 1.0 M

**pH** = 3.0 ± 0.02

**Gelatin** = 0.1 %

<table>
<thead>
<tr>
<th>Concentration of Lysine (moles)</th>
<th>log $ \frac{I}{I_0} $</th>
<th>$ -E_{1/2} $ V</th>
<th>$ F_0 (x) \times 10^3 $</th>
<th>$ i (x) $</th>
<th>$ F_2 (x) $</th>
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<tr>
<td>0.050</td>
<td>0.92</td>
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<td>--</td>
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<td>1.364</td>
<td>0.0014</td>
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<td>0.200</td>
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<td>0.600</td>
<td>0.92</td>
<td>1.886</td>
<td>0.045</td>
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<td>0.800</td>
<td>0.92</td>
<td>1.886</td>
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<td>75.14</td>
<td>18.5</td>
</tr>
</tbody>
</table>
### Table 3.2

**Pr (III), Nd (III) - Glycine System**

Concentration of the Metal Ion \( = 0.5 \text{ mM} \)

\[
\text{pH} \quad = 2.75 \pm 0.72
\]

Concentration of KCl \( = 1.0 \text{ M} \)

Gelatin \( = 0.01 \text{ %} \)

<table>
<thead>
<tr>
<th>Concentration of Glycine (moles)</th>
<th>Log ( C_x )</th>
<th>( - (\Gamma_{1/2})_c ) for Pr (III)</th>
<th>( - (\Gamma_{1/2})_c ) for Nd (III)</th>
</tr>
</thead>
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<td>0.0000</td>
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<td>1.31</td>
<td>1.831</td>
</tr>
<tr>
<td>0.0025</td>
<td>3.60</td>
<td>1.838</td>
<td>1.793</td>
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<td>0.0050</td>
<td>3.30</td>
<td>1.84</td>
<td>1.799</td>
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<td>0.0075</td>
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<td>0.0100</td>
<td>3.00</td>
<td>1.848</td>
<td>1.810</td>
</tr>
<tr>
<td>0.0125</td>
<td>2.99</td>
<td>1.850</td>
<td>1.817</td>
</tr>
<tr>
<td>0.0150</td>
<td>2.82</td>
<td>1.852</td>
<td>1.821</td>
</tr>
<tr>
<td>0.0175</td>
<td>2.75</td>
<td>1.855</td>
<td>1.824</td>
</tr>
<tr>
<td>0.0200</td>
<td>2.69</td>
<td>1.860</td>
<td>1.828</td>
</tr>
<tr>
<td>0.0250</td>
<td>2.60</td>
<td></td>
<td>1.830</td>
</tr>
</tbody>
</table>
### Table 3.3

**Co (III) - IDA - System**

<table>
<thead>
<tr>
<th>Concentration of Metal Ion</th>
<th>= 0.5 mM</th>
<th>pH</th>
<th>= 3.0 ± 0.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of K 1</td>
<td>= 1.0 M</td>
<td>Gelatin</td>
<td>= 0.01 M</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration of IDA (moles)</th>
<th>$I_d$ (div)</th>
<th>$E_{1/2}$ V</th>
<th>$\log I$</th>
<th>$F_0(x)$</th>
<th>$F_1(x)$</th>
<th>$F_2(x)$</th>
</tr>
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<td>0.00</td>
<td>102</td>
<td>1.85</td>
<td>--</td>
<td>--</td>
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</tr>
<tr>
<td>0.0005</td>
<td>98</td>
<td>1.864</td>
<td>0.2173</td>
<td>5.36</td>
<td>0.87</td>
<td>1.83</td>
</tr>
<tr>
<td>0.0015</td>
<td>96</td>
<td>1.866</td>
<td>0.2233</td>
<td>6.92</td>
<td>0.39</td>
<td>1.93</td>
</tr>
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<td>0.0020</td>
<td>94</td>
<td>1.894</td>
<td>0.3354</td>
<td>187.5</td>
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<td>3.9</td>
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<tr>
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<td>92</td>
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<td>0.3448</td>
<td>618.14</td>
<td>24.68</td>
<td>4.0</td>
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<td>0.0030</td>
<td>92</td>
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<td>0.3448</td>
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<td>83.96</td>
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<tr>
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<td>0.3543</td>
<td>8397.0</td>
<td>207.67</td>
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### Table 3.4

**Pr (III), Nd (III) - IDA System**

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<th>pH</th>
<th>Gelatin</th>
</tr>
</thead>
<tbody>
<tr>
<td>= 0.5 mM</td>
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<td>= 0.01 %</td>
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<tr>
<td>Concentration of KCl</td>
<td>= 1.0 M</td>
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<table>
<thead>
<tr>
<th>Concentration of IDA (mole)</th>
<th>Log $E_x$</th>
<th>$(-E_{1/2})_c$ for Pr (III)</th>
<th>$(-E_{1/2})_c$ for Nd (III)</th>
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<tbody>
<tr>
<td>0.00000</td>
<td>-</td>
<td>1.810</td>
<td>1.790</td>
</tr>
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<td>0.00025</td>
<td>- 3.60</td>
<td>1.828</td>
<td>1.810</td>
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<td>- 3.30</td>
<td>1.830</td>
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<td>1.842</td>
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<tr>
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<td>- 2.82</td>
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<td>1.832</td>
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<tr>
<td>0.00175</td>
<td>- 2.75</td>
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<tr>
<td>0.00250</td>
<td>- 2.60</td>
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<td>1.840</td>
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<tr>
<td>Concentration of Metal ion</td>
<td>pH</td>
<td>Concentration of KCl</td>
<td>pH</td>
</tr>
<tr>
<td>----------------------------</td>
<td>----</td>
<td>----------------------</td>
<td>----</td>
</tr>
<tr>
<td>Ce (III), Pr (III) and Nd (III) - NTA SYSTEM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 mM</td>
<td>3.0 ± 0.02 for Ce(III) - NTA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 M</td>
<td>2.75 ± 0.02 for Pr (III) - NTA</td>
<td></td>
<td></td>
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<tr>
<td>0.01 %</td>
<td>1.08</td>
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<table>
<thead>
<tr>
<th>Concentration of NTA (mole)</th>
<th>Log $C_x$</th>
<th>$-\left(\frac{E_{1/2}}{c}\right)_{\text{Ce (III)-NTA}}$</th>
<th>$-\left(\frac{E_{1/2}}{c}\right)_{\text{Pr (III)-NTA}}$</th>
<th>$-\left(\frac{E_{1/2}}{c}\right)_{\text{Nd (III)-NTA}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00000</td>
<td>-</td>
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<td>1.810</td>
<td>1.790</td>
</tr>
<tr>
<td>0.00025</td>
<td>- 3.60</td>
<td>1.850</td>
<td>1.820</td>
<td>1.810</td>
</tr>
<tr>
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<tr>
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<td>1.832</td>
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<tr>
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<td>1.825</td>
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<td>- 2.69</td>
<td>1.910</td>
<td>1.855</td>
<td>1.840</td>
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<tr>
<td>Concentration of Metal ion</td>
<td>pH = 3.0 ± 0.02 for Ce (III) BENZOATE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration of KCl</td>
<td>pH = 2.40 ± 0.02 for Pr (III), Nd (III) BENZOATE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gelatin</td>
<td></td>
<td></td>
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<table>
<thead>
<tr>
<th>Concentration of Benzoate (moles)</th>
<th>Log $C_x$</th>
<th>$-(E_{1/2})_c$ for Ce (III)-</th>
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<tbody>
<tr>
<td></td>
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<td>BENZOATE</td>
</tr>
<tr>
<td>0.00000</td>
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<td>pH</td>
<td>Concentration of KCl</td>
</tr>
<tr>
<td>---------------------------</td>
<td>----</td>
<td>----------------------</td>
</tr>
<tr>
<td>0.5 mM</td>
<td>3.0 ± 0.02</td>
<td>1.0 M</td>
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</table>

**Table 3.7**

Ce (III), Pr (III) and Nd (III) - Protocatechuic Acid System

<table>
<thead>
<tr>
<th>Concentration of Protocatechuic Acid (mM)</th>
<th>Log Cx</th>
<th>-((E_{1/2})) for Ce (III)&lt;br&gt;-((E_{1/2})) for Pr (III)&lt;br&gt;-((E_{1/2})) for Nd (III)</th>
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</thead>
<tbody>
<tr>
<td>0.0010</td>
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<td>1.850&lt;br&gt;1.819&lt;br&gt;1.790</td>
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<td>-3.30</td>
<td>1.870&lt;br&gt;1.812&lt;br&gt;1.810</td>
</tr>
<tr>
<td>0.0050</td>
<td>-3.00</td>
<td>1.872&lt;br&gt;1.830&lt;br&gt;1.812</td>
</tr>
<tr>
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<td>1.874&lt;br&gt;1.832&lt;br&gt;1.820</td>
</tr>
<tr>
<td>0.0020</td>
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<td>0.0025</td>
<td>-2.60</td>
<td>-</td>
</tr>
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<td>0.0030</td>
<td>-2.52</td>
<td>1.876&lt;br&gt;1.842&lt;br&gt;1.830</td>
</tr>
<tr>
<td>0.0035</td>
<td>-2.45</td>
<td>1.876&lt;br&gt;1.846&lt;br&gt;1.840</td>
</tr>
<tr>
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<td>1.880&lt;br&gt;1.850&lt;br&gt;1.858</td>
</tr>
<tr>
<td>0.0050</td>
<td>-2.30</td>
<td>1.886&lt;br&gt;1.860&lt;br&gt;1.860</td>
</tr>
<tr>
<td>Concentration of Salicylate (mole)</td>
<td>$I_d$ (div)</td>
<td>$E_{1/2}$ V</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>------------</td>
<td>-------------</td>
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<tr>
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<td>1.89</td>
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<tr>
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<td>0.55</td>
<td>1.92</td>
</tr>
<tr>
<td>Concentration of Salicylate (moles)</td>
<td>( \log C_x )</td>
<td>(- \left( \frac{E_{1/2}}{c} \right)_c ) for Pr (III) Salicylate</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>---------------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
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<td>- 2.69</td>
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<td>0.00250</td>
<td>- 2.50</td>
<td>1.865</td>
</tr>
<tr>
<td>0.00300</td>
<td>- 2.52</td>
<td>1.870</td>
</tr>
<tr>
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<td>- 2.45</td>
<td>1.872</td>
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<td>- 2.30</td>
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45. M.S. Mayadeo and S.S. Purohit,

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52. B. C. Bhuyan and G. N. Dubey,

53. B. C. Bhuyan and G. N. Dubey,

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55. T. A. Mhaske and K. N. Munshi,

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