CHAPTER THREE

POLAROGRAPHY OF SIMPLE AND MIXED COMPLEXES OF In(III), Eu(III) AND Nd(III).

> Introduction.
> Survey of Literature.
> Experimental Profile.
> Data and Schemes.
> Results & Discussion.
> References.

INTRODUCTION

Polarographic study of coordination compounds in its own right has recognized a specialized field\(^1\). Complexes are the compounds that contain a central metal atom or ion, usually a metal surrounded by a cluster of ions or molecules. Complexes with one kind of ligand are known a simple binary complexes (single or plural) where as, in which more than one type of ligand is bound to one metal ion. are termed as mixed ligand complexes. [Ternary]. For Metal : Ligand system using polarographic measurements, it is possible to determine the degree of formation, distribution and stability constant of all the species present in solution. The stability of ternary complexes may be influenced by certain direct or indirect
effect between the two ligands simultaneously bound to the central metal ion, charge neutralisation, steric factor, covalent bond formation, hydrophobic ligand-ligand interaction, hydrogen bonding, \( \Pi \)-bonding, charge transfer reaction, stacking interaction and the cooperative effects\(^2\text{-}^7\).

The complex compounds play an essential role in pharmaceuticals and chemical industries\(^8\text{-}^{15}\). The scope of chemistry of coordination compounds is wide. Both binary and ternary complexes have gained a lot of importance during recent past because they provide a model for various biological reactions and charge transfer electrode reactions. Introduction of certain metal into azo dyes used for better colour dye and produce higher resistance to fading. The study of metallic soap has been a subject of intense investigation. It is well known fact that metal ion solutions associated with water molecule form coordination linkage through oxygen atom\(^{16}\). New ligand can be introduced in place of water molecule by a certain tunneling or by a bridge mechanism\(^{17}\). During the last two decades several aspects of the coordination chemistry have gained new dimensions\(^{18\text{-}20}\). The mission of the present study is as under.

i. Use of polarographic methods for the complexation studies of rare earth as they produce difficulties due to their high negative reduction potentials.
ii. To determine the stoichiometry and stability constant of some simple and mixed complexes.

iii. To investigate overall mechanism of ternary complex formation in solution with its/their electrode reactions and distributions.

SURVEY OF LITERATURE.

Fortunately metal ions may be classified on the basis of the inertness of their complexes. Taube has discussed the hexavalent complexes. The complexation equilibria of lanthanide (III) cation have been studied mainly with the oxygen donor or Oxygen-nitrogen donor. The polarographic examinations of the cobalt (III) complex of ethylenediamine tetra acetic acid have been carried by Souchay and Faucher. Garg and Arya reported the complexes of La(III), Sm(III), Eu(III) and Yb(III) with diethylene triamine penta acetic acid, triethylene tetraamine hexaacetic acid and tetraethylene penta amine hexa acetic acid. Saxena et al. have reported the stepwise stability constants of La(III), Ce(III), Pr(III) and Sm(III) complexes of N, N'Bis (2-hydroxy ethyl) glycine and several other metal complexes of amino acid. Potentiometric studies on trivalent Pr, Nd, Sm, Gd and Dy complexes with substituted napthaquinone have been carried out by Rao and Reddy. Rao and Satyanarayan have made spectrophotometric studies on lanthanide(III) complexes with PAN in aquo-ethanol media. Literature reports the recent developments on
the reaction mechanism of complex formation along with stability constant under various conditions. Polarographic studies on the composition and stability of complexes of some tetracycline with uranyl ion in aqueous medium have been reported. Formation of U(VI) and Th(IV) complexes with cromotropic acid in solution has been studied by Prabhu and Coworkers. Effect of solvent on stability of complexes, thermodynamic analysis and complexation mechanism have been reported respectively in the literature. The driving forces in the formation of ternary complexes viz. statistical reasons, neutralisation of charges in mixed ligand complexes, steric factors and formation of π bonds etc. have been discussed by Sigel. Kostraminkhim and Rastvorov have calculated the stability constants of rare earth complexes with organic ligands. Daga et.al. have performed the studies of complexes of La(III), Pr(III), Sm(III) and Gd(III) using Irving-Rossotti technique. Longova and Meshkova have studied the complexation of transition metals with azodyes using spectrophotometric and conductometric technique. Stability constants and thermodynamic parameter of aspartic acid with rare earth have been determined potentiometrically. Whereas solid complexes were prepared by Farooq et.al. Pitre and Lavale critically examined the interaction of Sm(III)
with diethylene triamine penta acetic acid on DME and reported the species of the distributed ions, electrode reactions and formation constants of Sm\(^{2+}\)-DTPA complex under different experimental conditions. Binary complexes of In(III) with citric acid using potentiometric and high frequency titration techniques were reported by Ryabchikov and Marov. Ion exchange method has been utilized to study In(III) complexes with aminopolycarboxylic acid. Munshi and Sarin have reported the stepwise stability constants of In(III) complexes with mercapto, hydroxy, amino substituted analogs of succinic and propionic acids, thiosalicylic acid and salicylic acid etc. using potentiometric technique. Polarographic results on binary complexes of In(III) with salicylic acid and anthranilic acid have been reported by Pitre. Chitale and Pitre have reported Ce(III), Pr(III) and Nd(III) complexes with glycine, IDA, NTA, EDTA and DTPA using polarographic methods. Polarographic behaviour of metal ions viz. In(III) and Cd(II) in presence of polyethylene glycol in hydrochloric acid has been reported. Characterisation and formation constants of Lanthanide series have been studied by Khan et.al. Schiff bases and carbonyl compound behave as very good ligand with rare metals because of presence of basic group -C N. The protonation constants have been evaluated by shrinivasala and Mishra. Carey and Martell have
investigated the formation of mixed ligand complexes of U(IV) with ethylenediamine tetraacetic acid and nitrilotriacetic acid as primary ligands and salicylic acid as secondary ligand. Mixed Ligand 1:1:1 chelates of Th(IV) containing EDTA as primary ligand and amino acid like glycine, α-alanine and valine etc. as secondary ligands have been studied potentiometrically and their stability constants have been reported. Ramunas et al. reported the stabilities of trivalent metal complexes of phenolic ligands related to N-N' Bis (2-hydroxy benzyl) ethylenediamine N-N diacetic acid [HBED]. The charge neutralisation results in enhanced stability of ternary complexes was observed by Condike et al. Stability constants of ternary complexes have been determined pH-metrically and the role of steric effect is more clearly brought about in ternary system. Pitre et al. reported some mixed ligand system on DME. Gour et al. have studied mixed complexes of some transition metals with organic ligands on DME. Khurana and Gupta have also reported ternary complexes of some transition metals polarographically. Duley et al. have studied mixed complexes with some thio compounds on DME and Singh et al. have reported mixed complexes with some N-O donor ligands. Lavale et al. reported polarographic studies on the mixed ligand complexes of
In(III) with 2-2¹ bipyridyl urea and thioureia system. It is also reported in the literature about mixed ligand systems that the stability of mixed O,N donor ligand is midway between those of pure O,O and N, N donor ligands⁸⁰-⁸⁶. Ln(III) - EDTA - discarboxylate [where Ln=La(III), Ce(III), Pr(III), Nd(III) or Sm(III)], Ln(III) - MTA- discarboxylate, heterochelates in which dependence of solution stabilities on the size of chelate ring formed with discarboxylate has been observed in the literature⁸⁷-⁸⁹. Potentiometric and spectrographic method have been used by Mukhometzyanov et.al⁹⁰ for the study of Nd(III) complexes with N,N¹ bis (2-hydroxyethyl) ethylenediamine and N,N¹ disuccinic acid. Determination and extraction of indium and gallium complexes with bromopyrogallol red anthranilic acid have been done by various worker⁹¹-⁹⁶. Chitale et.al.⁹⁷ reported complexes of Nd(III) with immuno-diacetic acid and nitrilotriacetic acid however, the extraction of lanthanide as mixed ligand complexes reported by Krishnamurthy and Satyanarayana⁹⁸. Extractive spectrophotometric determination of indium alongwith the composition of Indium-complex is reported in the literature⁹⁹. Acrylic acid and crotonic acid have been used as a ligand for the study of complexes of Cd(II), Zn(II), Ni(II), Co(II) and U(IV)¹⁰⁰. Literature reveals the some reports on stability constant of the binary complexes of Nd(III) and Pr(III) with some aliphatic and
aromatic acids using polarographic measurements\textsuperscript{101-103}. Polarographic study and thermodynamic parameter of cyclohexyl thio-glyconate and hexyl thio-glyconate with In(III) in aqueous ethanol media has been reported by Gupta and Rao\textsuperscript{104}. A correlation of spectra and redox properties of some mixed ligand complexes has been discussed by Nigam et.al\textsuperscript{105}. Literature reports on various physico-chemical methods used for the study of complexations\textsuperscript{106-112}. Quarternary complexes, mostly of lighter lanthanides have been studied using NTA, EDTA and CDTA as complexones\textsuperscript{113-115}. Relative stabilities of some mixed complexes have been reported by Sharma et.al\textsuperscript{116}. The general observation is that the ternary complexes are more stable than the corresponding quarternary complexes\textsuperscript{117-118}. Even though many contradictory reports exist in literature on polarographic reduction of In(III) in various supporting electrolytes\textsuperscript{120-123}, an investigation on toxicity of indium has shown that it possesses potentially toxic properties\textsuperscript{124}. Further, because of its increasing industrial use\textsuperscript{125} and use as neutron moderators or reflectors\textsuperscript{126} author's interest on chemistry of indium has been stimulated. He planned to study electrochemical behaviour of In(III) and its simple and mixed complexes\textsuperscript{127-128}.

Polarographic studies on rare earth complexes involves certain difficulties. Since trivalent lanthanones
have a high negative reduction potential, similar to those of alkali metals, there is a possibility of secondary reactions with the medium, which may mask the primary wave. In the recent year much interest has been shown in the complexes of rare earth with aminopolycarboxylic acid due to their possible application in laser material.\textsuperscript{129-131} A perusal of literature on coordination chemistry of lanthanone reveals that there is a tremendous need of investigation. The present work has been undertaken to study on the binary and ternary complexes of Eu(III) and Nd(III) using polarographic measurements\textsuperscript{132-134}. This reveals the nature and structure of the species formed. A great deal of information may be gathered on the extent of interaction of metal ions and complexing agents in solution and about the distribution of species formed.

EXPERIMENTAL PROFILE

An automatic Eligo-lab DC recording polarograph model CL-25 D with recorder model LR-101 P was used to record the polarogram. Purified hydrogen gas was bubbled through the test solution before recording. All polarograms were recorded at \(24 \pm 1^\circ\) C. The capillary of DNE a 'm' value of 2.3733 \(\text{mg sec}^{-1}\) and a drop time 3.0 sec \(\text{drop}^{-1}\) at 40 cm. effective height of mercury column \([m^{2/3} t^{1/6} = 2.316 \text{ mg}^{2/3} \text{ sec}^{-1/2}]\) was used. The pH measurements were made on Toshniwal pH-meter model CL-46
with an assembly of glass and calomel electrode. Digital polarograph Toshniwal- model CLO-2B was also used to study some binary and ternary complexes. The pH of the test solutions was adjusted with dil. HCl/NaOH solution. KCl[1.0 Mol dm$^{-3}$] as a supporting electrolyte and gelatin [0.01 %] as a maximum suppressor were used during experimentation.

All the chemicals used were of AnalaR/BDH grade and their solutions were prepared in bidistilled water. 0.01M solutions of Eu(III) and Nd(III) were prepared by dissolving a weighed amount of their respective oxide [Eu$_2$O$_3$ - Rare earth product Ltd/India, Nd$_2$O$_3$-BDH/England] in minimum amount of hydrochloric acid and their subsequent evaporation to dryness and finally the residue was extracted in bidistilled water and standardized$^{135-136}$. The In(III) solution was prepared by dissolving InCl$_3$.3H$_2$O [BDH/England] in double distilled water and its concentration was checked amperometrically.$^{137}$ A solution of gelatin was freshly prepared whenever it was used. The ionic strength was kept constant $\mu$=1.0 using potassium chloride [BDH/England] solution. The required solution of crotonic acid [CA] and acrylic acid [AA] have been prepared as per requirments. Other chemicals used were of analytical grade. The experimental sets were prepared using definite amount of metal ion and Ligand at the
optimum condition of pH, μ, conc. temp etc. The polarograms were recorded and results have been enlisted in tables 3.1 to 3.7 and schemes 3.1, 3.2 and 3.3. In (III) and Eu (III) complexes with CA and AA have been studied at pH 4.5, the average pKa value of both CA and AA, moreover, the reduction is found to be reversible at the said pH. However, in case of Nd (III), the studies have been performed at pH = 2.50 as Nd (III) and its complexes produce reversible reduction wave, at higher pH > 5.0, the precipitation occurs.
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Ligand</th>
<th>Ratio</th>
<th>Complex species</th>
<th>Stability constant logβ values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Acrylic acid</td>
<td>1:3</td>
<td>[In(AA)₃]</td>
<td>log B₀₁ = 4.52</td>
</tr>
<tr>
<td>2.</td>
<td>Crotonic acid</td>
<td>1:1</td>
<td>[In(CA)⁺²]</td>
<td>log B₁₀ = 2.92</td>
</tr>
<tr>
<td>3.</td>
<td>Crotonic acid</td>
<td>1:2</td>
<td>[In(CA)₂⁺]</td>
<td>log B₂₀ = 3.95</td>
</tr>
<tr>
<td>4.</td>
<td>Crotonic acid</td>
<td>1:3</td>
<td>[In(CA)₃]</td>
<td>log B₃₀ = 5.50</td>
</tr>
<tr>
<td>5.</td>
<td>Crotonic acid</td>
<td>1:4</td>
<td>[In(CA)₄⁻]</td>
<td>log B₄₀ = 6.10</td>
</tr>
</tbody>
</table>

Table 3.1

STABILITY CONSTANTS OF In(III) BINARY COMPLEXES WITH ACRYLIC ACID (AA) AND CROTONIC ACID (CA)

pH = 2.5 ± 0.02  μ = 1.0 M  Temperature = 25 ± 1°C
<table>
<thead>
<tr>
<th>CA (M)</th>
<th>i_d (UA)</th>
<th>-E_k (V SCE)</th>
<th>F_oo[x,y] x10^{-4}</th>
<th>F_{10}[x,y] x10^{-5}</th>
<th>F_{20}[x,y] x10^{-6}</th>
<th>F_{30}[x,y] x10^{-7}</th>
<th>F_{40}[x,y] x10^{-9}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>7.20</td>
<td>0.650</td>
<td>1.82</td>
<td>3.35</td>
<td>5.42</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.050</td>
<td>7.03</td>
<td>0.660</td>
<td>5.92</td>
<td>9.80</td>
<td>15.60</td>
<td>23.31</td>
<td>-</td>
</tr>
<tr>
<td>0.075</td>
<td>6.98</td>
<td>0.674</td>
<td>15.17</td>
<td>18.12</td>
<td>22.35</td>
<td>34.50</td>
<td>4.45</td>
</tr>
<tr>
<td>0.100</td>
<td>6.80</td>
<td>0.681</td>
<td>61.30</td>
<td>60.32</td>
<td>58.30</td>
<td>54.32</td>
<td>5.28</td>
</tr>
<tr>
<td>0.125</td>
<td>6.62</td>
<td>0.687</td>
<td>142.80</td>
<td>114.07</td>
<td>89.68</td>
<td>68.50</td>
<td>5.39</td>
</tr>
<tr>
<td>0.150</td>
<td>6.60</td>
<td>0.689</td>
<td>280.12</td>
<td>186.00</td>
<td>122.22</td>
<td>79.00</td>
<td>5.33</td>
</tr>
</tbody>
</table>

A = 1.24 \times 10^4, \quad B = 1.8 \times 10^5, \quad C = 3.2 \times 10^6, \quad D = 1.3 \times 10^7, \quad E = 5 \times 10^9

\log A = 4.09, \quad \log B = 5.25, \quad \log C = 6.50, \quad \log D = 7.11, \quad \log E = 9.69.
Table - 3.3

POLAROGRAPHIC CHARACTERISTICS AND F_{ij} (X,Y) FUNCTIONS FOR [In(III)-(CA)-(AA)] SYSTEM

In(III) = 1.0 mM, J_A = 1 M KCL, (AA) = 0.4, pH = 4.5, E_{b} = -0.572 V vs. SCE.

<table>
<thead>
<tr>
<th>CA (mM)</th>
<th>i_{d}</th>
<th>-E_{b}</th>
<th>F_{00}(x,y) \times 10^{-4}</th>
<th>F_{10}(x,y) \times 10^{-5}</th>
<th>F_{20}(x,y) \times 10^{-6}</th>
<th>F_{30}(x,y) \times 10^{-7}</th>
<th>F_{40}(x,y) \times 10^{-9}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>6.81</td>
<td>0.660</td>
<td>6.02</td>
<td>4.35</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.050</td>
<td>6.30</td>
<td>0.671</td>
<td>21.58</td>
<td>32.82</td>
<td>58.13</td>
<td>16.15</td>
<td>2.5</td>
</tr>
<tr>
<td>0.075</td>
<td>6.21</td>
<td>0.684</td>
<td>122.93</td>
<td>158.10</td>
<td>205.80</td>
<td>20.78</td>
<td>2.7</td>
</tr>
<tr>
<td>0.100</td>
<td>6.05</td>
<td>0.690</td>
<td>290.40</td>
<td>284.80</td>
<td>280.72</td>
<td>23.14</td>
<td>2.5</td>
</tr>
<tr>
<td>0.125</td>
<td>6.02</td>
<td>0.701</td>
<td>635.00</td>
<td>504.48</td>
<td>402.38</td>
<td>28.03</td>
<td>2.3</td>
</tr>
<tr>
<td>0.150</td>
<td>5.83</td>
<td>0.705</td>
<td>1508.70</td>
<td>1003.10</td>
<td>666.12</td>
<td>41.00</td>
<td>2.6</td>
</tr>
</tbody>
</table>

A = 5.2 \times 10^4, \quad B = 2.2 \times 10^5, \quad C = 3.8 \times 10^6, \quad D = 9 \times 10^7, \quad E = 2 \times 10^9,

Log A = 4.71, \quad Log B = 5.34, \quad Log C = 6.57, \quad Log D = 7.95, \quad Log E = 9.30.
Table - 3.4

STABILITY CONSTANTS OF Eu(III) BINARY COMPLEXES WITH ACRYLIC ACID
(AA) AND CROTONIC ACID (CA)

pH = 2.5±0.02  \( \lambda = 1.0M \)  Temperature = 25±1°C

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Ligand</th>
<th>Ratio</th>
<th>Complex Species</th>
<th>Stability Constant log ( \beta ) Values.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Acrylic acid</td>
<td>1:1</td>
<td>([\text{Eu(AA)}]^2+)</td>
<td>( \log \beta_{01} = 1.62 )</td>
</tr>
<tr>
<td>2.</td>
<td>Crotonic acid</td>
<td>1:1</td>
<td>([\text{Eu(CA)}]^2+)</td>
<td>( \log \beta_{10} = 1.90 )</td>
</tr>
<tr>
<td>3.</td>
<td>Crotonic acid</td>
<td>1.2</td>
<td>([\text{Eu(CA)}_2]^+)</td>
<td>( \log \beta_{20} = 2.71 )</td>
</tr>
</tbody>
</table>
Table 3.5

Polarographic Measurements and $F_{ij}$ Functions of
Eu(III) - Crotonic Acid - Acrylic Acid System

Temp. = 25±1°C, $\mu = 1.0$ M, $\langle\text{AA}\rangle = 0.2$ M, $E_1 = -0.69$ V vs. SCE, $pH = 4.5$

<table>
<thead>
<tr>
<th>$C_x$</th>
<th>0.00</th>
<th>0.02</th>
<th>0.04</th>
<th>0.06</th>
<th>0.08</th>
<th>0.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CA]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mol dm$^{-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-E_\frac{1}{2}$</td>
<td>0.770</td>
<td>0.782</td>
<td>0.790</td>
<td>0.796</td>
<td>0.801</td>
<td>0.805</td>
</tr>
<tr>
<td>V vs SCE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A = 2.0,  B = 700,  C = $2 \times 10^5$

$\log B_{11} = 3.81$ or  $B_{11} = 6457$
Table - 3.6
STABILITY CONSTANTS OF Nd(III) BINARY COMPLEXES WITH ACRYLIC ACID (AA)
AND CROTONIC ACID (CA)

\[ \text{pH} = 2.5 \pm 0.02 \quad \mu = 1.0M \quad \text{Temperature} = 25 \pm 1^\circ \text{C} \]

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Ligand</th>
<th>Ratio</th>
<th>Complex Species</th>
<th>Stability Constant log B Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Acrylic acid</td>
<td>1:1</td>
<td>([\text{Nd(AA)}]^2+)</td>
<td>(\log B_{01} = 2.55)</td>
</tr>
<tr>
<td>2.</td>
<td>Acrylic acid</td>
<td>1:2</td>
<td>([\text{Nd(AA)}]^+)</td>
<td>(\log B_{02} = 5.35)</td>
</tr>
<tr>
<td>3.</td>
<td>Acrylic acid</td>
<td>1:3</td>
<td>([\text{Nd(AA)}]_3)</td>
<td>(\log B_{03} = 7.85)</td>
</tr>
<tr>
<td>4.</td>
<td>Crotonic acid</td>
<td>1:1</td>
<td>([\text{Nd(CA)}]^2+)</td>
<td>(\log B_{10} = 2.92)</td>
</tr>
<tr>
<td>5.</td>
<td>Crotonic acid</td>
<td>1:2</td>
<td>([\text{Nd(CA)}]^+)</td>
<td>(\log B_{20} = 5.48)</td>
</tr>
<tr>
<td>6.</td>
<td>Crotonic acid</td>
<td>1:3</td>
<td>([\text{Nd(CA)}]_3)</td>
<td>(\log B_{30} = 8.51)</td>
</tr>
</tbody>
</table>
### Table 3.7

**Polarographic Characteristics and $F_{ij}(X,Y)$ Functions for Nd (III) Crotonate-Acrylate Mixed System**

Nd (III) = 1.0 mM, $\lambda = 1.0$ M (KCl), pH = 2.50 ± 0.02, Temperature = 25 ± 1°C

Acrylic acid = 0.002 M (Fixed)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Concentration of Crotonic acid (div) $(M) \times 10^{-3}$</th>
<th>$i_{d}$</th>
<th>$-E_{k}$ V vs. Hg pool</th>
<th>$F_{\infty}(X,Y)$</th>
<th>$F_{10}(X,Y)$ $\times 10^{-3}$</th>
<th>$F_{20}(X,Y)$ $\times 10^{-5}$</th>
<th>$F_{30}(X,Y)$ $\times 10^{-9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.0</td>
<td>47.0</td>
<td>1.742</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>1.0</td>
<td>38.0</td>
<td>1.750</td>
<td>4.47</td>
<td>2.47</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>1.5</td>
<td>36.5</td>
<td>1.758</td>
<td>10.55</td>
<td>5.70</td>
<td>18.00</td>
<td>0.47</td>
</tr>
<tr>
<td>4.</td>
<td>2.0</td>
<td>35.0</td>
<td>1.764</td>
<td>22.18</td>
<td>10.09</td>
<td>35.45</td>
<td>1.22</td>
</tr>
<tr>
<td>5.</td>
<td>2.5</td>
<td>35.5</td>
<td>1.770</td>
<td>47.44</td>
<td>18.18</td>
<td>60.72</td>
<td>1.99</td>
</tr>
<tr>
<td>6.</td>
<td>3.0</td>
<td>32.0</td>
<td>1.774</td>
<td>69.47</td>
<td>22.49</td>
<td>64.97</td>
<td>1.80</td>
</tr>
<tr>
<td>7.</td>
<td>4.0</td>
<td>30.0</td>
<td>1.778</td>
<td>132.92</td>
<td>32.73</td>
<td>74.33</td>
<td>1.58</td>
</tr>
<tr>
<td>8.</td>
<td>5.0</td>
<td>28.5</td>
<td>1.787</td>
<td>407.70</td>
<td>81.14</td>
<td>156.28</td>
<td>2.91</td>
</tr>
</tbody>
</table>

$A = 2.0, \quad B = 3000, \quad C = 1.11 \times 10^5, \quad D = 1.49 \times 10^9$
Table 3.8

Polarographic characteristics and $F_{ij}(X,Y)$ functions for Nd (III) crotonate-acrylate mixed system

Nd (III) = 1.0 mM, $\mu = 1.0 M(\text{KCl})$, pH = 2.5 ± 0.02, Temperature = 25 ± 1°C
Acrylic acid = 0.004 M (Fixed)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Concentration of Crotonic acid (M) x 10^3</th>
<th>$i_d$ (div.)</th>
<th>$-E^{\text{Hg}}_n$ V vs. Hg pool</th>
<th>$F_{00}(X,Y)$ x 10^-4</th>
<th>$F_{10}(X,Y)$ x 10^-6</th>
<th>$F_{20}(X,Y)$ x 10^-6</th>
<th>$F_{30}(X,Y)$ x 10^-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.0</td>
<td>47.0</td>
<td>1.742</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>1.0</td>
<td>34.0</td>
<td>1.764</td>
<td>25.67</td>
<td>0.57</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>1.5</td>
<td>33.5</td>
<td>1.772</td>
<td>59.04</td>
<td>2.60</td>
<td>10.68</td>
<td>0.05</td>
</tr>
<tr>
<td>4.</td>
<td>2.0</td>
<td>31.0</td>
<td>1.776</td>
<td>101.82</td>
<td>4.09</td>
<td>15.45</td>
<td>0.27</td>
</tr>
<tr>
<td>5.</td>
<td>2.5</td>
<td>30.5</td>
<td>1.784</td>
<td>267.99</td>
<td>9.92</td>
<td>35.68</td>
<td>1.03</td>
</tr>
<tr>
<td>6.</td>
<td>3.0</td>
<td>28.5</td>
<td>1.788</td>
<td>515.05</td>
<td>16.50</td>
<td>51.67</td>
<td>1.39</td>
</tr>
<tr>
<td>7.</td>
<td>4.0</td>
<td>27.0</td>
<td>1.796</td>
<td>1210.37</td>
<td>29.76</td>
<td>71.90</td>
<td>1.55</td>
</tr>
<tr>
<td>8.</td>
<td>5.0</td>
<td>26.0</td>
<td>1.800</td>
<td>2005.96</td>
<td>39.72</td>
<td>77.44</td>
<td>1.35</td>
</tr>
</tbody>
</table>

$A' = 20.0, \quad B' = 1.0 \times 10^4, \quad C' = 1.03 \times 10^7, \quad D' = 1.07 \times 10^{10}$.  

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FIG. 3.1(a,b) TYPICAL POLAROGRAMS OF:
A. 1.0 mM In(III) AND B. 1.5 mM Eu(III)
FIG. 3-2. WAVE HEIGHT PLOT AGAINST $\sqrt{h}$
FOR In (II) IN POTASSIUM CHLORIDE.
FIG. 3.3  $E_{1/2}$ vs $\log[CA]$ FOR $\text{In}(\text{III})$ - CROTONATE SYSTEM.

[DE-FORD AND HUME'S METHOD]
FIG 3.4: $E_{1/2}$ (VOLTS VS S.C.E.) AGAINST $\log[CA]$ 

LINGANE PLOT FOR $\text{Eu(III)}$-ACRYLATE SYSTEM.
FIG. 3.5: DISTRIBUTION DIAGRAM FOR Eu(III)-CROTONIC AICD SYSTEM.
Fig. 3-6: A typical polarogram of 2 mM Nd(III) in 0.4 M KCl at pH = 2.5.
FIG. 3.7: PLOT OF $-E_{1/2}^\circ$ vs $\log[CA]$ FOR Nd (III)-CA SYSTEM.
FIG. 3.8: A TYPICAL PLOT OF $F_i[X]$ VS $[X]$ FOR Nd(III) - CA SYSTEM.
Scheme - 3.1

In(III) - CROTONATE - ACRYLATE MIXED SYSTEM

6.10

In(III) $\xrightarrow{2.92} [\text{In(CA)}]^{+2} \xrightarrow{1.02} [\text{In(CA)}_2] \xrightarrow{1.55} [\text{In(CA)}_3] \xrightarrow{-0.60} [\text{In(CA)}_4]$ 

$\xrightarrow{6.06}$ 

$\xrightarrow{5.85}$ 

$\xrightarrow{2.93}$ 

$\xrightarrow{2.11}$ 

$[\text{In(CA)(AA)}]^+ \xrightarrow{0.21} [\text{In(CA)(AA)}_2]$ 

$\xrightarrow{7.12}$ 

$\xrightarrow{4.52}$ 

$\xrightarrow{2.60} [\text{In(CA)(AA)}] \xleftarrow{1.06} \xrightarrow{1.27} [\text{In(CA)(AA)}]$ 

(AA) = Acrylic Acid, (CA) = Crotonic Acid.
Scheme - 3.2

Eu(III) - CROTONATE - ACRYLATE MIXED SYSTEM

\[
\begin{align*}
\text{Eu(III)} & \quad \rightarrow \quad [\text{Eu(CA)}]^2+ \\
(AA) \quad 1.90 & \quad \rightarrow \quad [\text{Eu(AA)}]^2+ \\
2.71 & \quad \rightarrow \quad [\text{Eu(AA)}]^2+ \\
1.91 & \quad \rightarrow \quad [\text{Eu(CA)} \cdot (AA)]^+ \\
(AA) \quad 0.81 & \quad \rightarrow \quad [\text{Eu(AA)}]^2+ \\
1.10 & \quad \rightarrow \quad [\text{Eu(AA)}]^2+ \\
\end{align*}
\]

(AA) = Acrylic Acid, (CA) = Crotonic Acid.
Scheme - 3.3
Nd(III) - CROTONATE - ACRYLATE MIXED SYSTEM

[AA] = Acrylic acid, [CA] = Crotonic acid
RESULTS AND DISCUSSION

The polarographic reduction of In(III) has been studied mostly in acid solutions, fewer in alkaline medium and in non aqueous medium. In(III) yields well defined reversible polarographic three electron reduction wave in 1 mol·dm⁻³ KCl and 0.01 % gelatin [Fig. 3.1 a]. It is also observed that in presence of acrylate or crotonate ion the wave height is diffusion controlled as the plot of iₜ vs. Hⁿ is linear and passes through the origin [Fig. 3.2]. The slope of linear plot of \( \log \frac{i}{i_d-I} \) vs \( E_{de} \) lies in the range of 19-21 mV. which attributes to the reversible reduction of In(III) and its complexes on a DME.

A. Polarography of simple complexes of In(III) with Acrylate and Crotonate.

Composition and stability constants of simple complexes of In(III) with acrylic acid and crotonic acid were determined separately prior to the study of mixed system. Identical conditions were maintained in both simple and mixed system.

(i) In(III) - Acrylate system: With the addition of In(III) is shifted to more negative potential. The plot of \( E_{1/2} \) vs log [AA] is straight line, thereby showing formation of single complex. The composition and stability constant was determined by
Lingane's method\textsuperscript{150}. Table 3.1 reports the data on composition and stability constant of this system.

\[ \text{In}^{3+} + 3Y \rightleftharpoons [\text{In} (Y)_3 ] \] \hspace{1cm} \ldots \ldots (1)

\textbf{(ii) In(III) - Crotonate System:} In each of the test solution the concentration of In(III) was maintained constant at 1 mM while that of crotonic acid varied from 0.01 M to 0.1 M with subsequent increase of [CA]. It was observed that the \( E_h \) shifted to more electronegative value. The plot of \( E_h \) vs log [CA] is a smooth curve thereby showing the formation of successive complexes [Fig.3.3]. The composition and stability of this system is determined by DeFord and Hume's method\textsuperscript{151}. This revealed the formation of successive complexes \( [\text{In(CA)}]^{2+} , [\text{In(CA)}_2]^+ , [\text{In(CA)}_3] \& [\text{In(CA)}_4]^− \) with the stability constant value of \( \log B_{10} = 2.92, \log B_{20} = 3.95, \log B_{30} = 5.50 \) and \( \log B_{40} = 6.10 \). The reduction equilibria for the successive complexes are as under

\[ \text{In}^{3+} + \text{HX} \rightleftharpoons [\text{In(X)}]^{2+} + \text{H}^+ \] \hspace{1cm} \ldots \ldots (2)

\[ [\text{In(X)}]^{2+} + \text{HX} \rightleftharpoons [\text{In(X)}_2]^+ + \text{H}^+ \] \hspace{1cm} \ldots \ldots (3)

\[ [\text{In(X)}_2]^+ + \text{HX} \rightleftharpoons [\text{In(X)}_3 ]^+ + \text{H}^+ \] \hspace{1cm} \ldots \ldots (4)

\[ [\text{In(X)}_3 ]^+ + \text{HX} \rightleftharpoons [\text{In(X)}_4]^− + \text{H}^+ \] \hspace{1cm} \ldots \ldots (5)

Table 3.1 indicates that the complexes of In(III) with crotonate are more stable than with acrylate. The reported data on stability may bring to evaluate the
degree of formation and the percentage distribution of various complex species. The stability constants may also be calculated by Mihailov method\textsuperscript{152-153}.

**B. Polarography of Mixed Complexes of In(III) with Acrylate and Crotonate.**

In the study of mixed complexes, the concentration of stronger ligand [CA] was varied from 0.025M to 0.150M and that of weaker ligand [AA] was kept constant. $E_1$ values were found to be more negative than those obtained in case of binary system thereby showing formation of mixed complexes. The experiments were performed at two different concentrations of weaker ligand: acrylic acid, [AA] = 0.2 M and at [AA] = 0.4 M. The polarographic characteristic and $F_{ij}[XY]$ functions for the mixed system have been tabulated in table 3.2 and table 3.3. The constant $A$, $B$, $C$, $D$ were evaluated by Leden's extrapolation method\textsuperscript{154}. Schaap and McMaster's method has been applied to determine the composition and stability constant of mixed ligand complexes\textsuperscript{155}. Three mixed complexes viz. [In(CA)(AA)]$^+$, [In(CA)(AA)$_2$] and [In(CA)$_2$(AA)] with stability constant $\log P_{11} = 5.85$, $\log P_{12} = 6.06$ and $\log P_{21} = 7.12$ are found. The various equilibria involved in this mixed ligand system have been presented in scheme 3.1. The equilibrium constant for the disproportion reaction

$$2[\text{In(CA)}_2(\text{AA})] \rightleftharpoons \text{In(CA)}_3 + [\text{In(AA)}_2]^+ + \text{CA}^- \quad \text{..(8)}$$
is found to be -3.50. The large negative value clearly indicates preferential tendency of In(III) to form mixed ligand complex species over the simple binary complexes.

Polarography of Eu(III) on a dropping mercury electrode has been discussed in detail\textsuperscript{156}. Polarogram of Eu(III) in 1.0 mol dm\textsuperscript{-3} KCl is found to be quasireversible in nature [Fig. 3.1 b]. $E^F_Y$ has been calculated by Gelling's treatment\textsuperscript{157}. However, the reduction of Eu(III) in presence of crotonic acid or acrylic acid is found to be reversible and diffusion controlled. The slope of linear plots of log$(i/i_d-i)$ vs. $E_{de}$ has been found in order of 60 mV. whereas the plots of $i_d$ vs $h_{corr}$ have been found to be linear passing through origin.

C. Polarography of simple complexes of Eu(III) with Acrylate and Crotonate.

Composition and stability constants of simple complexes of Eu(III) with acrylic acid and crotonic acid were determined. Identical conditions were maintained in the studies with CA and AA.

\textbf{(i) Eu(III) - Acrylate System}: A plot of $E^F_Y$ vs. log [AA] is found to be a straight line. Lingane's method\textsuperscript{150} was applied to study the complex formed. Eu(III) forms 1:1 complex with acrylic acid.

$$-E^F_Y = \frac{RT}{nF} \log \frac{[\text{Acrylate}]}{[\text{red}]} + (p-q) \frac{RT}{nF} \log C_X \quad \text{...(6)}$$
Where \( B_{\text{ox}} \) and \( B_{\text{red}} \) are the dissociation constants.
p and q the number of ligand associated with Eu\(^{3+}\) and Eu\(^{2+}\) respectively. The slope gives the change in number of ligand bound to Europium (p-q). It is found to be \( \approx 1 \). Ratio of the constants comes out to be 1.62. Table 3.4 records the data on binary complexes.

(ii) Eu(III) - Crotonate System: A plot of \( E_1 \) vs log[CA] is found to be a smooth curve [Fig. 3.4], this indicates the formation of successive complexes. DeFord and Hume's method was applied to determine the stability constant of successive complexes. Two complex species with \([\text{Eu(CA)}]^{2+}\) and \([\text{Eu(CA)}_2]^+\) with stability constant of \( \log B_{10} = 1.90 \) and \( \log B_{20} = 2.71 \) have been observed. The distribution diagram for Eu(III)-crotonate system is shown in fig. 3.5.

D. Polarography of Mixed Complexes of Eu(III) with Acrylate and Crotonate.

In Eu(III)-crotonate-acrylate system, the acrylic acid concentration was kept constant at 0.2 M and crotonic acid concentration was varied from 0 to 0.1 M. The polarographic characteristic are tabulated in table 3.5. Method of Schaap and McMaster\(^{155}\) has been used to determine the value of stability constant of \([\text{Eu(III)}-(CA)-AA]\) which comes out to be 3.81. The tendency of Ligand to add and substitute to another ligand is given in scheme 3.2.
Polarography of Nd(III) on a DME has been discussed in details\textsuperscript{158}. Nd(III) gives a well defined reversible reduction wave in 0.1-1.0 mol dm\textsuperscript{-3} KCl and 0.01% gelatin in the range of pH 2.40 to 2.79\textsuperscript{159}. A typical polagram Nd(III) is shown in fig. 3.6. The slope of linear plots of log $i/i_d$ vs $E_{de}$ lies in the range of 19-21 mV indicating three electron reversible reduction of Nd(III) and its complex species.

E. Polarography of Simple Complexes of Nd(III) with Acrylate and Crotonate.

Composition and stability constants of Nd(III) complexes with acrylic acid and crotonic acid were studied separately under identical conditions.

(i) Nd(III) Acrylate System: With the addition of increasing amount of acrylic acid, $E_1$ of Nd(III) is shifted to more negative values, thus indicating complex formation. A plot of $E_1$ vs. log [AA] is smooth, thereby showing the formation of successive complexes. DeFord and Hume's method was applied to calculate overall stability constants of binary complexes. This revealed the formation of $[\text{Nd(AA)}]^{2+}$, $[\text{Nd(AA)}_2]^{+}$ and $[\text{Nd(AA)}_3]$ with stability constant values of log $P_{01}=2.55$, log $P_{02}=5.35$ and log $P_{03}=7.85$.

(ii) Nd(III)- Crotonate System: The cathodic shift in $E_1$ values alongwith the decrease in diffusion current with increasing concentration of crotonic acid
indicated complex formation of Nd(III) with crotonic acid. The plot of $E_1$ vs log [CA] was found to be smooth, thereby showing the formation of successive complexes [Fig. 3.7]. DeFord and Humes method was applied to evaluate the stability constants. Three complex species [Nd(CA)$_2$]$^{2+}$, [Nd(CA)$_3$] and [Nd(AC)$_3$] with log $\beta_{10} = 2.92$, log $\beta_{20} = 5.48$ and log $\beta_{30} = 8.51$ were observed. The polarographic data on binary complexes of Nd(III) have been reported in table 3.6.

F. Polarography of Mixed Complexes of Nd(III) Crotonate Acrylate System.

Schaap and McMaster's method was applied to study mixed complexes. Two concentrations of acrylic acid 0.002M and 0.004M were chosen for the study of mixed ligand system, where 1:1 and 1:2 complexes predominate. The concentration of crotonic acid varied from 0 mM to 5.0mM. A more negative shift in $E_1$ values, as compared to shift observed in absence of acrylate ion, was observed. This indicated the formation of mixed complexes. Polarographic data have been tabulated in table 3.7 and 3.8. Leden's extrapolation method was applied to calculate A, B, C and D. [Fig. 3.6]. The result revealed the formation of [Nd(AC)(AA)]$^+$ and [Nd(AC)$_2$(AA)] with formation constants log $\beta_{11} = 6.09$ and log $\beta_{21} = 8.62$. The mixing constant ($K_m$) and stability constant ($K_s$) for the reaction
\[ \frac{1}{2}[\text{Nd(CA)}_2]^+ + \frac{1}{2}[\text{Nd(AA)}_2]^+ \rightarrow [\text{Nd(CA)(AA)}]^+ \]

Which is a measure of relative stability of ternary complexes in solution as compared to the parent binary complexes have been calculated.\textsuperscript{160-161} The low values of \(K_m\) and \(K_s\) showed that the mixed complexes are more stable than binary complexes. Scheme 3 indicates the tendency of [CA] and [AA] to add and substitute to Nd(III) in complex formation.

The perusal of the above results on the study of complexation of In(III), Eu(III) and Nd(III) reveals to the fact that each of the metal ions forms simple and mixed complexes with said ligands. Aspects on methodic approach to the observed polarographic data, values of formation constants, mixing constant, stability constant etc. will be beneficial to the workers in coordination chemistry. The study of mixed ligand Nd(III) complexes using DME created a new driving forces, where the literature lacks with references on mixed ligand complexes of rare earth using polarographic measurements. Author's reading references and salient feature on polarographic data may be fruitful in the electrochemistry, laser
technology and neutron activation analysis. It is hoped that these findings may also prove to be of great importance in recent years not only to electrochemists but also to inorganic chemists, physicists and research workers interested in interdisciplinary analytical complexometry.
REFERENCES


41. Longova M., Simek Z., Chroma J. and Sommer L., Collection, 1988, 52, 4232.


111. Garg B.S. et.al., Polyhedron, 1988, 7-2, 147.


154. Leden I., Phys. Chem., 1941, 188.


