LIST OF PUBLICATIONS

(1) Polarographic study of binary and ternary complexes of In(III) with y-icoline and citraconic acid.

(2) Amperometric trace determination of Tb(III), Dy(III) and Er(III) with Alizarin-Red-S.

(3) Polarographic reduction of Er(III) complexes with iminodiacetic acid, Nitrilotriacetic acid, Ethylene diamine tetra-acetic acid and Diethylene triamine pentaacetatc acid on a d.m.e.

(4) Studies on mixed ligand complexes of In(III) with citraconic acid and Nicotinic acid.

(5) Electrometric studies of binary and ternary complexes of In(III) with y-Picoline and Nicotinic acid.
- Nisha Shrivastava and K.S.Pitre; J.Indian Chem. Soc.(Accepted for publication).

contd..
(6) Trace determination of Tb$^{3+}$, Dy$^{3+}$ and Er$^{3+}$ using 4-(2-Pyridylazo) Resorcinol (RAR) as an amperometric reagent.
- Nisha Shrivastava and K.S. Pitre; J. Indian Chem. Soc. (Accepted for publication)

(7) Polarographic reduction of Zn(II) in presence of Y-nicotine and nicotinic acid.
- Nisha Shrivastava and K.S. Pitre; J. Electrochem Soc. (India) (Communicated)

(8) Composition and formation constants of binary and ternary complexes of Zn(II) with Y-nicotine and citraconic acid.
- Nisha Shrivastava and K.S. Pitre; J. Indian Chem. Soc. (Communicated).

(9) Electrochemical behavior of Zn(II)-Citroconate-Nicotinate ternary system on a d.m.e.
- Nisha Shrivastava and K.S. Pitre; J. Indian Acad. Sci. (Communicated)
Polarographic Study of Binary and Ternary Complexes of In(III) with \( \gamma \)-Picoline and Citraconic Acid

Nisha Shrivastava and K.S. Pitre

Department of Chemistry, Dr. Harisingh Gour Vishwavidyalaya, Sagar 470 003 (M.P)

Polarograms of In(III)-\( \gamma \)-Picoline-Citraconate system at pH 4.5 \( \pm \) 0.02 in aqueous medium has been used to study the complexes. Deford and Hume's method has been used to study the stoichiometry and formation constants of binary complexes and Schaap and Mcmaster's method was used for the study of ternary complexes. It has been observed that [In(\( \gamma \)-Pico)]\( \gamma \)-Citraconate system at pH 4.5 \( \pm \) 0.02 in aqueous medium has been used to study the complexes. Deford and Hume's method has been used to study the stoichiometry and formation constants of binary complexes and Schaap and Mcmaster's method was used for the study of ternary complexes. It has been observed that [In(\( \gamma \)-Pico)\( \gamma \)-Pico]\( \gamma \)-Pico] and [In(\( \gamma \)-Pico)\( \gamma \)-Pico] \( \gamma \)-Pico] ternary complexes are formed with formation constants \( \log \beta_1 = 4.66 \), \( \log \beta_2 = 6.22 \) and \( \log \beta_2 = 7.40 \) respectively.

Ever since the work of Schaap and Mcmasters an increasing number of research papers have appeared, on the use of polarographic method for the study of stoichiometry and formation constants of mixed ligand complexes. In continuation of the work in our laboratory (2-6) the present paper describes the results of polarographic study on binary and ternary complexes of In(III) with \( \gamma \)-Picoline and Citraconic acid.

**EXPERIMENTAL**

Di-Sodium salt of citraconic acid was prepared and used as a ligand. Potassium chloride (1M) was used as supporting electrolyte. Indium ion concentration in polarographic solution was 1 mM. Reagent grade chemicals and double distilled water are used throughout. Deford and Hume's method was used to study the stoichiometry and formation constants of binary complexes of In(III) with \( \gamma \)-Picoline and Citraconic acid ligands separately.

For the study of ternary complexes of In(III) with these ligands Schaap and Mcmaster's method was applied.

A.C.I.C. (India) polarograph was used to record the current-voltage curves. The capillary used had \( \sqrt{2} \) = 2.316 mg sec\(^{-1}\) in 1 M potassium chloride at 45 cm effective height of mercury column. The pH of the test solutions was adjusted to pH 4.5 \( \pm \) 0.02 using dil HCl/NaOH solution. An Ellico digital pH meter model LI-120 was used to read the pH of the test solutions. Purified nitrogen gas was passed through the solutions before recording polarograms. All the observations were made at 27.5 \( \pm \) 0.1°C.

**RESULTS AND DISCUSSION**

In (III) gave a three electron, reversible, and diffusion controlled reduction wave in all the media studied. The slopes of linear plots of \( \log \frac{1}{E_1-E_0} \) Vs E were of the order of 21 \( \pm \) 1 mV

**TABLE 1**

<table>
<thead>
<tr>
<th>[( \gamma )-Picoline] ( -E/) mv</th>
<th>( 1 d ) (div.)</th>
<th>( F_0[X] )</th>
<th>( F_1[X] ) ( X 10^{-1} )</th>
<th>( F_2[X] ) ( X 10^{-3} )</th>
<th>( F_3[X] ) ( X 10^{-5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 \ 0.00</td>
<td>610</td>
<td>64</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2 \ 0.01</td>
<td>618</td>
<td>62</td>
<td>2.636</td>
<td>16.36</td>
<td>-</td>
</tr>
<tr>
<td>3 \ 0.02</td>
<td>624</td>
<td>58</td>
<td>5.685</td>
<td>23.42</td>
<td>4.21</td>
</tr>
<tr>
<td>4 \ 0.03</td>
<td>634</td>
<td>57</td>
<td>18.97</td>
<td>59.90</td>
<td>14.96</td>
</tr>
<tr>
<td>5 \ 0.04</td>
<td>640</td>
<td>56</td>
<td>38.36</td>
<td>93.40</td>
<td>19.60</td>
</tr>
<tr>
<td>6 \ 0.05</td>
<td>646</td>
<td>53</td>
<td>81.79</td>
<td>161.58</td>
<td>29.31</td>
</tr>
<tr>
<td>7 \ 0.06</td>
<td>650</td>
<td>52</td>
<td>133.2</td>
<td>220.30</td>
<td>34.22</td>
</tr>
</tbody>
</table>

\( \log \beta_1 = 2.17 \)

\( \log \beta_2 = 3.00 \)

\( \log \beta_3 = 5.54 \)


34-4(1985) 276
**TABLE 3**

**POLAROGRAPHIC CHARACTERISTICS AND F_{ij} FUNCTIONS OF**

In (III) - Citraconate-γ-Picoline mixed system

In (III) = 1 mM, \( \mu = 0.1 \) [KCl], pH = 6.5 ± 0.02, Temp. = 27.5 ± 0.1°C

( \( E^0_{\Gamma} \)) = 0.610 V Vs SCE; \( t_d \) (in div.) = 64 γ-Picoline = 0.1 M (fixed)

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Concentration of citraconate</th>
<th>E 1/2 (V Vs SCE)</th>
<th>t_d (div.)</th>
<th>( F_{00}[X,Y] ) ( \times 10^{-2} )</th>
<th>( F_{10}[X,Y] ) ( \times 10^{-4} )</th>
<th>( F_{20}[X,Y] ) ( \times 10^{-6} )</th>
<th>( F_{30}[X,Y] ) ( \times 10^{-8} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01</td>
<td>-0.630</td>
<td>58</td>
<td>11.48</td>
<td>1.48</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
<td>-0.638</td>
<td>57</td>
<td>29.81</td>
<td>9.90</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>0.03</td>
<td>-0.654</td>
<td>55</td>
<td>201.1</td>
<td>63.70</td>
<td>4.56</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>0.04</td>
<td>-0.664</td>
<td>52</td>
<td>686.3</td>
<td>169.07</td>
<td>29.75</td>
<td>3.18</td>
</tr>
<tr>
<td>5</td>
<td>0.05</td>
<td>-0.670</td>
<td>50</td>
<td>1141</td>
<td>226.20</td>
<td>35.24</td>
<td>3.64</td>
</tr>
<tr>
<td>6</td>
<td>0.06</td>
<td>-0.672</td>
<td>48</td>
<td>1897</td>
<td>314.50</td>
<td>44.08</td>
<td>4.51</td>
</tr>
</tbody>
</table>

**γ-Picoline 0.2m (fixed)**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Concentration of citraconate</th>
<th>E 1/2 (V Vs SCE)</th>
<th>t_d (div.)</th>
<th>( F_{00}[X,Y] ) ( \times 10^{-2} )</th>
<th>( F_{10}[X,Y] ) ( \times 10^{-4} )</th>
<th>( F_{20}[X,Y] ) ( \times 10^{-6} )</th>
<th>( F_{30}[X,Y] ) ( \times 10^{-8} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.01</td>
<td>-0.634</td>
<td>56</td>
<td>19.05</td>
<td>-</td>
<td>9.01*</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>0.02</td>
<td>-0.640</td>
<td>56</td>
<td>38.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>0.03</td>
<td>-0.654</td>
<td>55</td>
<td>199.5</td>
<td>59.83</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>0.04</td>
<td>-0.668</td>
<td>52</td>
<td>1096</td>
<td>269.00</td>
<td>52.25</td>
<td>8.56</td>
</tr>
<tr>
<td>11</td>
<td>0.05</td>
<td>-0.672</td>
<td>50</td>
<td>1821</td>
<td>360.20</td>
<td>60.04</td>
<td>8.40</td>
</tr>
<tr>
<td>12</td>
<td>0.06</td>
<td>-0.676</td>
<td>48</td>
<td>3029</td>
<td>501.50</td>
<td>73.58</td>
<td>9.26</td>
</tr>
</tbody>
</table>

A = 10;

B = 5000;

C = 1700.00;

D = 28000.00

A' = 20;

B' = 6000;

C' = 1800.00;

D' = 8000.00

**REFERENCES**


and the plots of $i_d$ vs $h_{corr}$ were linear passing through origin.

**BINARY COMPLEXES**

Deford and Hume’s treatment of the observed polarographic data was used to study the binary complexes. Table 1 and 2 represent the $F_i(x)$ functions and other relevant data for the In(III)-$\gamma$-Picoline and In(III)-Citraconate systems. The data in the table reveal the formation of three binary complexes of In(III) with each of the two ligands.

**TERNARY COMPLEXES**

For the polarographic studies on the ternary In-Citraconate-$\gamma$-Picoline system, two concentrations of $\gamma$-Picoline were so chosen that in predominantly exists as 1:1 and 1:2 complexes respectively. The concentration of citraconate was varied from 0.0 M and 0.1 M and that of $\gamma$-Picoline fixed at 0.1 M and 0.2 M respectively. A more electronegative shift in the $E_{mv}$ values as compared to shift observed in absence of citraconate ion, was observed. This indicated the formation of ternary complexes. Schaap and Mccmaster’s treatment has been used. The $F_{ij}$ functions and $A$, $B$, $C$ and $D$ constants have been tabulated (Table 3). The results revealed the formation of three mixed complexes viz. $[\text{In(CA)}]^{-}, [\text{In(CA)}_2(\gamma\text{Pico})]$ and $[\text{In(CA)}(\gamma\text{Pico})]$ with formation constants $\log \beta_1 = 4.66$, $\log \beta_2 = 6.22$ and $\log \beta_3 = 4.70$ respectively.

The mixing constant $K_M$ and stabilisation constant for the reaction:

$$\frac{1}{2} \text{[In(\gamma-Pico)]}_2 + \frac{1}{2} \text{[In(CA)]}_2$$

$$= [\text{In(CA)}(\gamma\text{Pico})]^{-}$$

(Which is a measure of relative stability of the ternary complexes in solution as compared to the parent binary complexes) have been calculated (8) by the relation $K_M = B_{12}/B_{20}$ and $\log K_S = \log K_M - \log 2$, respectively. The values of $\log K_M = 1.3133$ and that of $\log K_S = 1.0123$ show that the ternary complexes are little more stable than the binary complexes. A scheme showing the tendency of a ligand to add to a complex and to substitute another ligand is given below:

![Diagram of ternary complex formation]

**Table 2**

In (III) – Citraconate system; Values of $F_i(x)$ Functions

$\text{In(III)} = 1 \text{mM, } \mu = 0.1 \text{[KCl]}, \text{pH} = 3.5 \pm 0.02, \text{Temp.} = 27.5 \pm 0.1^\circ \text{C}$

All Potentials are with respect to SCE.

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>[Citraconate] $E_{mv}$</th>
<th>$i_d$ (div.)</th>
<th>$F_2(x)$</th>
<th>$F_1(x)$</th>
<th>$F_2(x) \times 10^{-3}$</th>
<th>$F_3(x) \times 10^{-5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>610</td>
<td>64</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>624</td>
<td>60</td>
<td>5.495</td>
<td>44.9</td>
<td>4.95</td>
</tr>
<tr>
<td>3</td>
<td>0.02</td>
<td>630</td>
<td>59</td>
<td>23.45</td>
<td>112.2</td>
<td>36.12</td>
</tr>
<tr>
<td>4</td>
<td>0.03</td>
<td>638</td>
<td>56</td>
<td>31.70</td>
<td>102.3</td>
<td>20.77</td>
</tr>
<tr>
<td>5</td>
<td>0.04</td>
<td>652</td>
<td>56</td>
<td>156.3</td>
<td>388.2</td>
<td>87.06</td>
</tr>
<tr>
<td>6</td>
<td>0.05</td>
<td>654</td>
<td>56</td>
<td>223.9</td>
<td>445.8</td>
<td>81.16</td>
</tr>
<tr>
<td>7</td>
<td>0.06</td>
<td>660</td>
<td>47</td>
<td>475.3</td>
<td>790.5</td>
<td>125.08</td>
</tr>
</tbody>
</table>

$\log \beta_1 = 2.60$ $\log \beta_2 = 3.70$ $\log \beta_3 = 6.04$

*J. Electrochem. Soc. India.*
AMPEROMETRIC TRACE DETERMINATION OF Tb$^{3+}$, Dy$^{3+}$ AND Er$^{3+}$ WITH ALIZARIN RED S

Nisha Srivastava and K.S. Pitre

Department of Chemistry, Dr. H.S. Gour Vishwavidyalaya, Sagar (M.P.)

Amperometric titration procedure has been successfully employed for
the trace determination of Tb$^{3+}$, Dy$^{3+}$ and Er$^{3+}$ in aqueous and partially nonaqueous media. The titrations have been carried out at -0.7 V
vs. Hg pool; pH = 4.5, and p = 0.1. The current-volume plots indicated
a metal to ARS complexation ratio of 1:2 in each case. Absorptio-
metric studies made on the above complexation, also confirmed the said ratio. Interference to the titration by other ions is examined.

A survey of literature reveals that Alizarin Red-S (Abbr. as ARS) has been widely used as a complexometric spectrophotometric, and pH metric reagent
[1-5]. In continuation of the work in our laboratory on trace determination of rare earths with reagents of modern analytical importance[6-11],
the present paper describes the results of amperometric titration of Tb$^{3+}$, Dy$^{3+}$ and Er$^{3+}$ with ARS using a dme-Hg pool electrode system.

EXPERIMENTAL

All the chemicals used were of Analytical/Extrapure quality. Tb$^{3+}$, Er$^{3+}$ and Dy$^{3+}$ solutions were prepared
and standardised[9]. The solution of ARS was prepared by dissolving a requisite quantity of the reagent in double distilled water and standardised
by the procedure of Larson and Hirozawa[12]. A manually operated polarograph with a multiflex
galvanometer (Sens. 8.1x10$^{-9}$ amp/dv) was used for
amperometric titrations, using dme-Hg pool electrode system. An Ellic-digital pH meter model L1-
120 was used for measuring pH of the test solutions. The metal ligand complexation equilibrium
was studied using a double beam sample chamber
GCA/MCPherson Spectrophotometer model Eu 707-11.

Amperometric titrations were done by preparing
sets of solutions containing different concentra-
tion of ARS in 0.1 mole dm$^{-3}$ KCl as supporting electrolyte. The pH of these experimental sets
was adjusted at 4.5 using acetate buffer.

RESULTS AND DISCUSSION

ARS gives a well defined cathodic reduction
wave[13] in 0.1 mol. dm$^{-3}$ KCl and acetate buffer at
pH 4.5 (Fig.1). The diffusion current is propor-
tional to the concentration of ARS. For amperome-
tric titrations, test solution containing a known
concentration of ARS in 0.1 mol dm$^{-3}$ KCl and ac-
etate buffer (pH = 4.5) was taken in a titration
cell. The plateau potential of the polarogram for
ARS, i.e. -0.7 V vs. Hg pool, was applied. At this
potential the titrated metal ions are not reduced
(Fig. 1). The standard solution of metal ion

Fig. 1 (A) Polarogram of 1 m M Alizarin Red S in
0.1 m KCl at pH = 4.5

(B) Polarogram of 2 m M metal (Tb$^{3+}$, Dy$^{3+}$
or Er$^{3+}$) in 0.1 m KCl at pH = 4.5

(pH = 4.5) was added drop by drop from 1 cm$^{3}$micro-
burette. A violet red precipitate was observed
in the test solution. The current was noted on a
multiflex galvanometer. The galvanometer deflec-
tion after making necessary volume correction was
plotted against the volume of metal added when a L
shaped curve was observed. Typical graph is given
in Fig. 2. The end point indicated a metal to
ligand ratio of 1:2 which is in excellent agree-
ment with the results reported in the literature
[10,11]. A reversed L shaped curve is obtained by
taking rare earths as titrate and ARS as titrant
under the above mentioned experimental conditions.
It is also observed that the amperometric titra-
tion procedure holds good in 25% ethanol water
medium as well.

Interference Study

For the study of the effect of diverse ions, known
amount of foreign ions were added to a definite

**TABLE 1**

**AMPEROMETRIC DETERMINATION OF TERBIUM, DYSPROSEUM AND EREBIUM**

WITH ALIZARIN RED S AT - 0.7 V vs MERCURY POOL

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Approximate Terbium (mg)</th>
<th>% Error</th>
<th>Dyssproseum (mg)</th>
<th>% Error</th>
<th>Eriberum (mg)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Taken</td>
<td>Found</td>
<td>Taken</td>
<td>Found</td>
<td>Taken</td>
<td>Found</td>
</tr>
<tr>
<td>1</td>
<td>0.25</td>
<td>0.7980</td>
<td>0.7880</td>
<td>-0.25</td>
<td>0.8125</td>
<td>0.8098</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>1.5800</td>
<td>1.5750</td>
<td>-0.31</td>
<td>1.6250</td>
<td>1.6212</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>2.3700</td>
<td>2.3754</td>
<td>+0.22</td>
<td>2.4375</td>
<td>2.4452</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>3.1600</td>
<td>3.1670</td>
<td>+0.22</td>
<td>3.2500</td>
<td>3.2388</td>
</tr>
<tr>
<td>5</td>
<td>1.25</td>
<td>3.9500</td>
<td>3.9612</td>
<td>+0.28</td>
<td>4.0625</td>
<td>4.0782</td>
</tr>
<tr>
<td>6</td>
<td>1.5</td>
<td>4.7400</td>
<td>4.7250</td>
<td>-0.30</td>
<td>4.8750</td>
<td>4.8608</td>
</tr>
<tr>
<td>7</td>
<td>1.75</td>
<td>5.5300</td>
<td>5.5532</td>
<td>+0.42</td>
<td>5.6875</td>
<td>5.7124</td>
</tr>
</tbody>
</table>

Standard Deviation = 0.21%  
Coefficient of Variance = 0.45

Standard Deviation = 0.18%  
Coefficient of Variance = 0.38

Standard Deviation = 0.25%  
Coefficient of Variance = 0.35

The measurements were carried out at pH 4.5 and wave length 540 μm. Absorption studies were made within 1 hr of preparing the sets as it was observed that in nearly three hours gelatinous precipitation takes place. The metal ligand stoichiometric ratio with all the three titled metal ions with ARS is found to be 1:2 (Fig.3) which confirms the ratio observed by authors in the amperometric titration procedure. To evaluate the equilibrium constant, the molar ratio method and non-linear

**Fig. 2** Amperometric titration curve of Tb with ARS concentration of ARS solution taken in cell = 0.015 M 10 ml (concentration of Tb solution = 0.02 M ml)

ammount of ARS in test solution and then the titurations were performed following the procedure described above. It was observed that hundred fold concentration of the ions, NH₄⁺, K⁺, Na⁺, Cl⁻, ClO₃⁻, SO₄²⁻, NO₃⁻, and CH₃COO⁻ do not interfere in the titration procedure (Table 2). However, small amounts of Ag⁺, Pb²⁺, Bi³⁺, Al³⁺, Fe³⁺ VO₃⁻, Cr₂O₇²⁻, MoO₄²⁻ and CO₃²⁻ ions interfere in the titration appreciably.

Absorption Studies on Metal Ligand Equilibrium

Vosburgh & Cooper s[14] method was used to study the complex formed. The visible absorption spectra of 0.1 m MOL dm³ of ARS at pH = 4.5 consists of a single maximum at 420 μm and ARS complexes with each of the titled metals at 540 μm. The shift in λmax may be attributed to the formation of metal complex. To study the stoichiometry of the complex, job's method of continuous variation[5] has been successfully applied. The measurements were carried out at pH 4.5 and wave length 540 μm. Absorption studies were made within 1 hr of preparing the sets as it was observed that in nearly three hours gelatinous precipitation takes place. The metal ligand stoichiometric ratio with all the three titled metal ions with ARS is found to be 1:2 (Fig.3) which confirms the ratio observed by authors in the amperometric titration procedure. To evaluate the equilibrium constant, the molar ratio method and non-linear

**Fig. 3** Job's plot for composition at 54 μl.
### Table 2

**Amperometric Determination of Terbium, Dysprosium and Erbium with ARS in Presence of Diverse Ions**

<table>
<thead>
<tr>
<th>Diverse ions added</th>
<th>Terbium 1.5800 mg Found</th>
<th>% Error</th>
<th>Dysprosium 1.6250 mg Found</th>
<th>% Error</th>
<th>Erbium 0.8363 mg Found</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺ (115 mg)</td>
<td>1.5816</td>
<td>+ 0.10</td>
<td>1.6204</td>
<td>- 0.28</td>
<td>0.8392</td>
<td>+ 0.34</td>
</tr>
<tr>
<td>K⁺ (195 mg)</td>
<td>1.5834</td>
<td>+ 0.21</td>
<td>1.6196</td>
<td>- 0.33</td>
<td>0.8316</td>
<td>- 0.56</td>
</tr>
<tr>
<td>NH₄⁺ (42.5 mg)</td>
<td>1.5738</td>
<td>- 0.39</td>
<td>1.6276</td>
<td>+ 0.16</td>
<td>0.8384</td>
<td>+ 0.25</td>
</tr>
<tr>
<td>Mg²⁺ (24.3 mg)</td>
<td>1.5708</td>
<td>- 0.58</td>
<td>1.6294</td>
<td>+ 0.27</td>
<td>0.8304</td>
<td>- 0.70</td>
</tr>
<tr>
<td>Zn²⁺ (32.69 mg)</td>
<td>1.5818</td>
<td>+ 0.11</td>
<td>1.6105</td>
<td>- 0.89</td>
<td>0.8344</td>
<td>- 0.22</td>
</tr>
<tr>
<td>Sn⁺⁺ (11.86 mg)</td>
<td>1.5698</td>
<td>- 0.65</td>
<td>1.6190</td>
<td>- 0.37</td>
<td>0.8348</td>
<td>- 0.17</td>
</tr>
<tr>
<td>Hg²⁺ (10 mg)</td>
<td>1.5910</td>
<td>+ 0.69</td>
<td>1.6184</td>
<td>- 0.40</td>
<td>0.8310</td>
<td>- 0.63</td>
</tr>
<tr>
<td>Cd²⁺ (11.24 mg)</td>
<td>1.5652</td>
<td>- 0.93</td>
<td>1.6209</td>
<td>- 0.25</td>
<td>0.8388</td>
<td>+ 0.29</td>
</tr>
<tr>
<td>Sb⁺⁺ (3.94 mg)</td>
<td>1.5704</td>
<td>- 0.60</td>
<td>1.6314</td>
<td>+ 0.39</td>
<td>0.8298</td>
<td>- 0.77</td>
</tr>
<tr>
<td>Zn²⁺ (3.19 mg)</td>
<td>1.5664</td>
<td>- 0.86</td>
<td>1.6410</td>
<td>+ 0.90</td>
<td>0.8412</td>
<td>+ 0.58</td>
</tr>
<tr>
<td>Ti⁴⁺ (10.2 mg)</td>
<td>1.5652</td>
<td>- 0.93</td>
<td>1.6158</td>
<td>+ 0.56</td>
<td>0.8296</td>
<td>- 0.80</td>
</tr>
</tbody>
</table>

The method of Job was employed. The conditional formation constants are found to be 10.51, and 10.13, 9.81 respectively for 1:2, Er³⁺: ARS, Tb³⁺: ARS and Dy³⁺: ARS complexes in solution.

### Statistical Treatment of the Data

Ultramicro and microgram quantities of Er³⁺, Tb³⁺ and Dy³⁺ have been determined by this amperometric procedure with ARS. The error in determination is found to be less than ±0.8% and coefficient of variation never exceeded 0.45.

### Acknowledgements

One of the authors (NS) is grateful to the U.G.C. and Government of M.P. for providing her a J.R.F. The authors are thankful to the Head of Chemistry Department, U.T.D. Sagar for providing necessary laboratory facilities.

### References


J. Electrochem. Soc. India

---

POLAROGRAPHIC REDUCTION OF Er (III) COMPLEXES WITH IMINODIACETIC ACID, NITROLOTRI ACETIC ACID, ETHYLENE DIAMINE TETRA ACETIC ACID AND DIETHYLENE TRIAMINE PENTA ACETIC ACID ON A d. m. e.

NISHA SHRIVASTAVA AND K. S. PITRE

Department of Chemistry, Dr. Harisingh Gour University, Sagar-470 003 (M. P.).

(Received 15 May, 1985)

In continuation to the work in our laboratory on Ce++, Pr++, Nd++, Gd++, etc. complexes with Glycine, IDA, NTA, EDTA and DTPA, using polarographic method\(^1\)-\(^3\), the present authors report the stoichiometry and stability constants of Er (III) complexes with IDA, NTA, EDTA and DTPA on the basis of the polarographic studies carried out according to above procedure.

EXPERIMENTAL AND DISCUSSION

Er (III) gives a well defined, reversible, three electron reduction wave in 0.1 M KCl at PH = 2.5 ± 0.02 and ƞ = 0.1 (KCl). The reduction of Er (III) and its complexes with each of the ligands under study (IDA, NTA, EDTA and DTPA) was found to be of diffusion controlled nature. The plots of \(i_\alpha vs \sqrt{b_{corr}}\) yields a straight line passing through the origin. The plots of \(\log \frac{1}{i_\alpha - i} vs E_{d.s.}\) for each of the polarogram were found to be linear with a slope of 20 ± 1 mV which indicates a reversible nature of the reduction wave of Er (III) and its complexes in each case.

Effect of Ligand Concentration: With increase of ligand concentration to metal test solution the half wave potential shifted to more electronegative values. Lingane\(^4\) treatment of the data revealed formation of 1:1 complexes of Er (III) with NTA, EDTA and DTPA, whereas indication of successive complex formation was observed in case of Er (III)—IDA system. Deford and Hume's\(^8\) method was therefore applied in this case, which revealed formation of 1:1 and 1:2 complexes. The order of formation constants is given in Table 1. The increased values of formation constants from IDA to DTPA may be explained on account of presence of acetic acid groups in increasing order from IDA to DTPA. The literature, however, records higher values for formation constants of the chelates under
study. The difference in formation constants may be assigned to lower pH value of the experimental sets.

**Table—1**

Formation constants of Sr (III) complexes with IDA, NTA, EDTA and DTPA.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>M : L ratio</th>
<th>Complex Species</th>
<th>log β</th>
</tr>
</thead>
<tbody>
<tr>
<td>IDA</td>
<td>1 : 1</td>
<td>[Sr(IDA)]⁺</td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td>1 : 2</td>
<td>[Sr(IDA)]⁻</td>
<td>8.59</td>
</tr>
<tr>
<td>NTA</td>
<td>1 : 1</td>
<td>[Sr(NTA)]</td>
<td>6.7</td>
</tr>
<tr>
<td>EDTA</td>
<td>1 : 1</td>
<td>[Sr(EDTA)]⁻</td>
<td>7.5</td>
</tr>
<tr>
<td>DTPA</td>
<td>1 : 1</td>
<td>[Sr(DTPA)]²⁻</td>
<td>8.7</td>
</tr>
</tbody>
</table>

**REFERENCES**

STUDIES ON MIXED LIGAND COMPLEXES OF In (III) WITH CITRACONIC ACID AND NICOTINIC ACID

NISHA SHRIVASTAVA AND K. S. PITRE

Department of Chemistry, Dr. H. S. Gour University Sagar (M. P.).

(Received 15 May, 1985)

This paper reports the results of investigations on the mixed ligand complexes, of In-Citraconate-Nicotinate system, on a d.m.e.

EXPERIMENTAL AND DISCUSSION

Mono and di-sodium salts of In (III) and ligands (nicotinic acid and citraconic acid) were used to prepare experimental sets. 1M potassium chloride was used as base electrolyte to study the polarographic behaviour of In (III) (1 mM) binary and mixed complexation. All the observations were made at a constant ionic strength $\mu = 0.1$ (adjusted with potassium chloride); pH $= 4.5 \pm 0.02$ and at room temperature $27 \pm 0.5^\circ$.

Polarograms were recorded on a C.I.C. (India) polarograph. The capillary used had a m$^{2}$/s $t^{1/2}$ value equal to 2.136 mg$^{1/2}$/sec$^{1/2}$.

In (III) and its binary and ternary complexes under study are reversibly reduced at the d.m.e., involving three electrons. The slopes of linear plots of $\log \frac{i}{i_d - i}$ vs $E_{d}$ are of the order of $21 \pm 1$ mv. and the plots of $i_d$ vs $\sqrt{E_{d}}$ are linear and pass through origin, which shows that the reduction is diffusion controlled in each case.

Stoichiometry and formation constants of binary complexes of In (III) with nicotinic acid and citraconic acid by Lingane$^1$ treatment of the observed polarographic data revealed smooth curves for the plots of $E_{1/2}$ vs log (ligand), in each case, indicating formation of successive complexes. Deford and Hume$^2$ method was then applied to the said systems to calculate the stoichiometric ratio of metal : ligand complexation and formation constants.

The values obtained are given below:

**In (III)-Nicotinate System.**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>log $\beta_{10}$</td>
<td>2.30</td>
</tr>
<tr>
<td>log $\beta_{10}$</td>
<td>3.30</td>
</tr>
</tbody>
</table>

**In (III)-Citraconate System.**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>log $\beta_{20}$</td>
<td>2.60</td>
</tr>
<tr>
<td>log $\beta_{20}$</td>
<td>3.70</td>
</tr>
<tr>
<td>log $\beta_{m}$</td>
<td>6.04</td>
</tr>
</tbody>
</table>
Table I

<table>
<thead>
<tr>
<th>Concentration of citraconate (M)</th>
<th>$E_1/2$ (V vs SCE)</th>
<th>$id$ (div)</th>
<th>$F_{00}$ [XY]</th>
<th>$F_{10}$ [XY]</th>
<th>$F_{10}$ [XY]</th>
<th>$F_{20}$ [XY]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>-0.538</td>
<td>54</td>
<td>51.47</td>
<td>1.47</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>0.02</td>
<td>-0.644</td>
<td>54</td>
<td>62.52</td>
<td>16.78</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>0.08</td>
<td>-0.680</td>
<td>52</td>
<td>429.5</td>
<td>133.16</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>0.04</td>
<td>-0.676</td>
<td>52</td>
<td>2757</td>
<td>691.75</td>
<td>1027.5</td>
<td>81.87</td>
</tr>
<tr>
<td>0.06</td>
<td>-0.678</td>
<td>44</td>
<td>4178</td>
<td>829.00</td>
<td>1099.2</td>
<td>79.84</td>
</tr>
<tr>
<td>0.08</td>
<td>-0.680</td>
<td>40</td>
<td>5808</td>
<td>963.00</td>
<td>1138.3</td>
<td>73.05</td>
</tr>
</tbody>
</table>

$A^1 = 30$  $B^1 = 28000$  $C^1 = 7000,00$  $D^1 = 7000,000$

For the study of In (III)-citraconate-nicotinate system, the nicotinate concentration was fixed at 0.1M and 0.2M separately. All other experimental conditions were maintained the same as in the case of binary complexes. The citraconate concentration was varied from 0.0 M to 0.06 M in each case (table 1). A Schap and Mcmasters treatment of the data revealed the formation of three mixed complexes, viz. [In (CA) (NA)], [In (CA)$_2$ (NA)$_2$] and [In (CA) (NA)$_3$] with formation constants $\log \beta_{11} = 5.06$, $\log \beta_{12} = 6.29$ and $\log \beta_{13} = 5.11$ respectively. The mixing constant $K_M$ and stabilisation constant $K_s$ for the reaction:

$$\frac{1}{2} [\text{In (CA)}] + \frac{1}{2} [\text{In (NA)}] = [\text{In (CA) (NA)}],$$

which are related to the measure of relative stability of mixed complexes in solution over the parent binary complexes, are found to be as follows: $\log K_M = 1.5645$ and $\log K_s = 1.2635$. The positive values of these parameters indicate that the mixed complexes are little more stable than the binary complexes.

**SUMMARY**

Polarographic reduction of simple and mixed ligand complexes of In-citraconate-nicotinate system on a d.m.e. has been studied. Observed polarographic data, on Schap and Mcmasters treatment revealed formation of three mixed complexes, viz. [In (CA) (NA)], [In (CA)$_2$ (NA)$_2$] and [In (CA) (NA)$_3$] with formation constants $\log \beta_{11} = 5.06$, $\log \beta_{12} = 6.29$ and $\log \beta_{13} = 5.11$ respectively. The mixing constant ($\log K_M = 1.5645$) and stabilisation constant ($\log K_s = 1.2635$) have been calculated.

**REFERENCES**

Dear Sir/Madam,

I am to inform you that your Paper/s* No. 117/85 has/have been finally accepted for publication in the Journal of the Indian Chemical Society as an Article/Note.

*Electrometric Studies of nicotinic acid.

Yours truly,

Executive Editor.
Dear Sir/Madam,

I am to inform you that your Paper/s No. 72/65 has/have been finally accepted for publication in the Journal of the Indian Chemical Society as an Article/ a Note.

- Trace determination of ____________ reagent__

Yours truly,

Executive Editor.