2.1 Introduction.

2.1.1. Electrochemical techniques. Electro analytical chemistry encompasses a group of analytical techniques that are based on electrical properties of an analyte in solution, present in an electrochemical cell. The electro analytical techniques, broadly involve Bulk and Interfacial methods.

Scheme 2.1. Electro analytical techniques
Bulk methods deal with the various phenomena that take place in the bulk of the solution, while interfacial methods deal with a phenomenon that occurs at the electrode and solution interface. Further, the interfacial methods can be divided into two major categories, static (in which steady state or equilibrium or non polarized conditions are included) and dynamic or transient (in which polarized or diffusion controlled conditions are observed.) A brief classification is given in Scheme 2.1.

Table 2.1. Variable controlled/measured and information sought out of electro analytical techniques.

<table>
<thead>
<tr>
<th>Method</th>
<th>Controlled Variable</th>
<th>Measured Variable</th>
<th>Excitation Signal</th>
<th>Response Signal</th>
<th>Information Obtained</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potentiometry</td>
<td>( i = 0 )</td>
<td>E</td>
<td>Concentration</td>
<td>Potential</td>
<td>Concentration</td>
<td>Used mainly in analytical devices</td>
</tr>
<tr>
<td>Conductometry</td>
<td>( V(AC) )</td>
<td>( i(AC) )</td>
<td>( AC )-potential (1-100kHz)</td>
<td>( AC ) current</td>
<td>Resistance, Conductance Capacitance, Dielectric constant</td>
<td>---</td>
</tr>
<tr>
<td>Voltammetry</td>
<td>( E(t) )</td>
<td>( i )</td>
<td>Potential sweep</td>
<td></td>
<td>Current vs potential</td>
<td>Amount, D, ( E^0 ), Kinetics</td>
</tr>
<tr>
<td>Polarography</td>
<td>( E )</td>
<td>( i )</td>
<td></td>
<td>Current vs time</td>
<td>Amount, D, ( E^0 ), Kinetics</td>
<td>Especially useful in studies of surface species, higher sensitivity by use of superimposed square wave or potential pulses</td>
</tr>
<tr>
<td>Single-sweep</td>
<td>( E(t) )</td>
<td>( i )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclic-sweep</td>
<td>( E(t) )</td>
<td>( i )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotated-disk and ring disk electrodes</td>
<td>( E, \omega )</td>
<td>( i )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulse</td>
<td>( \Delta E(t) )</td>
<td>( \Delta i )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chronoamperometry</td>
<td>E-step</td>
<td>( i(t) )</td>
<td>Potential step</td>
<td>Current vs time</td>
<td>Amount, D, ( E^0 ), Kinetics</td>
<td>Used in mass-and charge-transfer rate measurements</td>
</tr>
<tr>
<td>Chronocoulometry</td>
<td>E-step</td>
<td>( \int i , dt )</td>
<td>Potential step</td>
<td>Coulombs vs time</td>
<td>Amount, D, ( E^0 ), Kinetics</td>
<td></td>
</tr>
<tr>
<td>Controlled potential electrolysis</td>
<td>( E )</td>
<td>( \int i , dt )</td>
<td>Potential step</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrolysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chronopotentiometry</td>
<td>( i )</td>
<td>( E(t) )</td>
<td>Current step</td>
<td>Potential vs time</td>
<td>Amount, D, ( E^0 ), Kinetics</td>
<td>Less frequently used</td>
</tr>
<tr>
<td>Galvanostatic</td>
<td>( i )</td>
<td>( E(t = 0) )</td>
<td>Current step</td>
<td>Potential vs time</td>
<td>Amount, D, ( E^0 ), Kinetics</td>
<td></td>
</tr>
<tr>
<td>Coulometric titrations</td>
<td>( i )</td>
<td>( (i/t)/F )</td>
<td>Current step</td>
<td>Potential vs time</td>
<td>Amount, D, ( E^0 ), Kinetics</td>
<td></td>
</tr>
</tbody>
</table>

The technological advancement has improved instrumentation, which overcome the limitations of classical techniques. These techniques are sensitive, selective, rapid and versatile. The various electro analytical techniques are cyclic voltammetry, linear sweep voltammetry, rotating disc electrode voltammetry, tafel plot, step-sweep functions, chronocoulometry, staircase voltammetry, taf polarography, differential pulse voltammetry and polarography, normal pulse voltammetry and polarography, differential normal pulse voltammetry, square wave voltammetry, multi-potential steps, AC voltammetry, phase selective
AC voltammetry, second harmonic AC voltammetry, AC impedance vs time/potential, linear sweep stripping voltammetry, normal pulse stripping voltammetry, AC stripping voltammetry, chronopotentiometry and miscellaneous techniques. According to the nature of signals involved, these techniques can be broadly classified as (1) Constant excitation signals, (2) Variable excitation signals of large amplitude, (3) Variable excitation signals of small amplitude and (4) Stripping techniques.

**Chrono methods.** If the electrical signals are dependent on time, then the electro analytical techniques are called chrono methods. They are chronoamperometry, chronopotentiometry and chronocoulometry. In chronoamperometry, the measuring electrical parameter is current when the process is initiated by a potential step, while in chronopotentiometry the measuring parameter is potential when the process is initiated by a current step. Alternatively, these time-dependant signals may be initiated by injection of a charge pulse rather than a step function. In such cases, the above methods are referred as coulostatic or cyclic potential steps respectively.

**Pulse methods.** A square wave is superimposed upon the normal slow DC polarographic sweep either by electronic superimposition of a square wave or by a mechanical or electrical switch that alter the electrode potential between two levels. All forms of pulse polarography have an advantage of greater sensitivity.

**Sweep techniques.** When the rate of voltammetric scan is increased above a few millivolts per second, the interface region that is the electrode does not have sufficient time to achieve stable quasi-equilibrium gradient with the bulk solution before the voltage is significantly changed. The best example of this technique is of cyclic voltammetry in which the direction of voltage scan is reversed (ramp returns almost invariably to the original potential and the excitation waveform is actually an isosceles triangle). Single sweep polarography,
triangular sweep polarography, fast liner sweep voltammetry etc. are the techniques come into this class.

**AC techniques.** In these techniques, periodic waveforms generally of low amplitude are superimposed upon a DC potential applied to an electrochemical cell. Any periodic waveform can be expressed as a Fourier series of different frequencies and phase angle. **AC** techniques are used in both polarography and voltammetry as well as in modes where no sweep is applied.

**Stripping techniques.** In this technique, the potential of an electrode is initially held for a relatively long period of time (the deposition step) during which material moves from the solution and accumulates/deposits onto the electrode. No measurement is being made during the deposition. The deposited material on the electrode may then be allowed to assume an equilibrium distribution or configuration at some other potential (the equilibrium step) and again no measurements are made. The third step in stripping technique, is an analytical step in which the deposited material is oxidized or reduced back into solution usually by voltammetry and there by determined. The anodic stripping voltammetry is highly sensitive technique, widely used for speciation analysis.

**Cyclic voltammetry.** Cyclic voltammetry has become an important and widely used electro analytical technique in many areas of chemistry. It is rarely used for quantitative determination, but it is widely used for the study of redox processes, in understanding reaction intermediates and for obtaining stability of reaction products.

This technique is based on varying the applied potential at a working electrode in both forward and reverse directions at some given scan rate while monitoring the current. For example, the initial scan could be in the negative direction to the switching potential. At that
point the scan would be reversed and run in the positive direction. Depending on the analysis, one full cycle, a partial cycle or a series of cycles can be performed.

The important parameters in a cyclic voltammograms are the peak potentials \((E_{pc}, E_{pa})\) and peak currents \((i_{pc}, i_{pa})\) of the cathodic and anodic peaks respectively. Cyclic voltammetry is carried out in quiescent solution to ensure the process is diffusion controlled. A three-electrode arrangement is used. Mercury film electrodes are used because of their good negative potential range. Other working electrodes include glassy carbon, platinum, gold, graphite and carbon paste.

**Chronopotentiometry.** It is an analytical method in which the potential of the indicating electrode is measured as a function of time while the current that passes through it is controlled at a constant value. The analytically useful variants of chronopotentiometry are those in which the potential is monitored after either a current-step signal or charge-step signal initiated. In this technique, the current flowing in the cell is instantaneously stepped from zero to some finite value. A typical chronopotentiogram shown in the figure is for the reaction \(O + ne^{-} \leftrightarrow R\). As the current pulse is applied, a sharp decrease in the potential as the double layer capacitance is charged until at which the oxidant is reduced. Then a fairly slow decrease in the potential is determined by the Nernst equation until the surface concentration of oxidant reaches to zero. The flux of oxidant to the surface is then no longer sufficient to maintain the applied current and the electrode potential again fall more sharply, until a further electrode process occurs. Sand\(^1\) worked out the theory of chronopotentiometric measurements. The study of heterogeneous kinetics is theoretically possible by this technique but not recommended due to the probability of double layer charge effects.

**Chronoamperometry.** Here, the current that flows through the indicating electrode is measured as a function of time, while the excitation signal usually a voltage, is either...
constant or some simple function of time. It employs three electrodes in a steady solution with a square wave function as the input for the working electrode. The potential difference between the working and reference electrode start at zero and no redox reaction can occur at the working electrode. The voltage then jumps immediately on the working electrode and the potential difference between working and reference electrode is great enough to induce a redox reaction at the working electrode. The resultant density gradient leads to a flow of oxidant toward the electrode and reluctant away from the electrode. This moving charge can be measured by an ammeter and is called diffusion current. The current response to this sweep in potential is characterized by an immediate jump in current, which drops off as the oxidant is depleted.

**Chronocoulometry.** In chronocoulometry the total charge is recorded as a function of time in this technique. Here the potential of the working electrode is changed instantaneously, and the charge-time response is recorded. The advantage of chronocoulometry over chronoamperometry is that since the charge is the integral of the current it retains at long time information about the value of the current at short times.

### 2.1.2. Electrochemistry of Eu(III)

Kolthoff and Lingane² have discussed the electrochemical features of lanthanide metal ions in its +3 oxidation state. The reduction of these metal ions seems to be an interesting problem because of their typical electronic structure. Only three lanthanide metal ions [Eu (III), Yb(III) and Sm(III)] have stable divalent ions therefore the reduction step is accessible for electrochemical investigation³. However, the cyclic voltammograms of Eu(III) recorded in perchloric acid, sodium chloride and potassium chloride show that the reduction of Eu(III) is found quasi reversible at HMDE⁴. The authors have narrated that the cathodic peak is sharp but anodic peak is rounded and diffusive. The reduction of Eu(III) at DME in the presence of different base electrolytes are also reported as totally irreversible⁵.

Thus, the electrochemistry of Eu(III)/Eu(II) couple at DME/HMDE/Pt and other electrodes have been the subject of a large number of investigations. Comprehensive studies are also reported by Misumi and Ide⁶, Vleck⁷, Gierst and Cornelissen⁸ and by Macero et.al.⁹. The main
interest in this system is due to the fact that the europium is the only one of the lanthanides that has a stable +2 state in aqueous solutions, and that the standard redox potentials, $E^\circ$, of that system is very close to the point of zero charge at the mercury when there is no specific adsorption.

It has been found that the reduction of Eu(III) at the DME is polarographically irreversible in most supporting electrolytes except in thiocyanate\textsuperscript{10}. An unstable Eu(II) intermediate of different electronic configuration from the reduced solutions has been postulated and the activation over potential associated with the electrochemical reaction has been attributed to a shielding effect caused by the 5s and 5p electrons\textsuperscript{11}. The utility of Kalouske (K-I and K-II) polarography in the investigation of the Eu(III)/Eu(II) system using variable electrode kinetics was studied by Kindrd and Philippir\textsuperscript{12} and suggested the reversibility of Eu(III)/Eu(II) reaction as evidenced by K-I/K-II curves increases in order of supporting electrolytes as ClO$_4^-$, < Cl$^-$, < NO$_3^-$, < Br$^-$, < I$^-$ and < SCN$^-$. The double anodic wave observed by Kinard\textsuperscript{12} at low ionic strength in perchlorate is explained as the double layer effect rather than in an intermediate in the reduction. An electrochemical behavior of Eu(III) in presence of halide and sulfate is assumed as\textsuperscript{13}

$$
M^{3+} + X^- \rightleftharpoons MX^{2+} \\
MX^2 + X^- \rightleftharpoons MX_2^+
$$

The reversible reduction of Eu(III) at DME in the presence of EDTA and in formate buffer has also been reported\textsuperscript{13} The electrode mechanism of Eu(III)/Eu(II) coupled reaction is shown by Sluyters et.al.\textsuperscript{14}.

The reduction of rare earth ions at DME has been investigated in a number of non-aqueous solvents. In DMF\textsuperscript{15,16} and DMSO\textsuperscript{16}, Sm(III), Eu (III) and Yb(III) show two steps reduction while the other rare earth ions exhibit only one. The detailed mechanism of M(III)/M(II) redox process for Sm(III) and Eu(III) cannot be regarded as established in non aqueous solvents and the electron transfer process seem rather slow in all solvents studied. Galus et.al.\textsuperscript{16} have studied the kinetics of Eu (III)/Eu (II) system at mercury electrode in aqueous, CH$_3$CN, DMF, DMSO and HMPA solvents and established order of the formal potential as CH$_3$CN< H$_2$O < DMF < DMSO < HMPA with the increase in solvation ability.
Europium(III) is found to be an excellent ideal system for elaborate studies, which behave from totally reversible to irreversible depending on the supporting electrolyte and/or the ligand present in the solution. It was established that the reversibility increase in order of supporting electrolytes $\text{ClO}_4^- < \text{Cl}^- < \text{NO}_3^- < \text{Br}^- < \text{I}^- < \text{SCN}^-$ and appears to correlate only with decreasing charge at the electrode surface owing to the increased specific adsorption of the anions. Further, comprehensive studies on the Eu (III)/Eu (II) couple at the dropping mercury electrode have been reported by many workers.

The influence of water and the effect of $[\text{H}^+]$ ion on Eu (III) electrode reduction in CH$_3$CN explained by Hush and Dyke as

\[
\begin{align*}
\text{Eu}^{3+} & \xrightarrow{\text{e}^-} \text{Eu}^{2+} \\
\text{Eu}^{2+} & \xrightarrow{\text{H}^+} \text{Eu}^{3+} + \frac{1}{2}\text{H}_2 \\
\text{Eu}^{3+} (\text{H}_2\text{O})_x (\text{CH}_3\text{CN})_y & \xrightarrow{} \text{Eu}^{3+} (\text{OH}) (\text{H}_2\text{O})_{x-1} (\text{CH}_3\text{CN})_y + \text{H}^+
\end{align*}
\]

The replacement of water molecules by CH$_3$CN within the coordination sphere of Eu (III) is a fast reaction, while its behavior in DMF as given below.

\[
\begin{align*}
\text{M}^{2+} & \xrightarrow{\text{H}_2\text{O}} \text{M}^{3+} + \text{OH}^- + \frac{1}{2}\text{H}_2 \\
(\text{DMF})_n\text{Sm}^{3+} (\text{H}_2\text{O}) & \xrightarrow{} (\text{DMF})_n\text{Sm}^{3+} (\text{OH}^-) + \text{H}^+ \\
\text{M} (\text{DMF})_{8}^{3+} + (n-8) \text{DMF} + \text{e}^- & \xrightarrow{} \text{M}(\text{DMF})_{n}^{2+}
\end{align*}
\]

The importance of lanthanides in understanding the behavior of many biomolecules and particularly the electrochemical behavior of Eu(III) metal ion has tempted us for investigation in depth.

2.2 Experimental.

2.2.1. Materials. All the chemicals used were of Analar/G.R. grade and procured from E. Merck or BDH. Tetraethyl ammonium tetra fluoro borate (TEABF$_4$), sodium perchlorate and Europium chloride (EuCl$_3$.6H$_2$O) was obtained from Aldrich Chemicals and M/s. Rare Earth India Ltd. respectively. A standard 0.1 M solution of EuCl$_3$.6H$_2$O was prepared in doubly distilled water, estimated by volumetric method and used to prepare experimental solutions as and when required.
An aqueous mixture of 0.1 N Na$_2$SO$_4$–H$_2$SO$_4$ (1 ≤ pH ≤ 2.5), 0.1N NaCl–HCl (1 ≤ pH ≤ 2.5) or 0.2N CH$_3$COONa–H$_2$SO$_4$/HCl (1 ≤ pH ≤ 4.5) as a buffer medium and a 0.1 M solution of LiCl, NaCl, KCl, NaClO$_4$ or Na$_2$SO$_4$ (at their own pH) as unbuffered medium were used.

A solution of 0.1 N (TEABF$_4$)/LiCl/NaClO$_4$ in (50:50, 70:30, 90:10 and 98:02) of DMF-H$_2$O/MeOH-H$_2$O/CH$_3$CN- H$_2$O were used as aquo-organic medium. The zero grade N$_2$ gas, purchased from IOLAR & Co., was further purified by passing successively through 15% pyrogallol in 40% KOH, H$_2$SO$_4$ and anhydrous silica gel.

2.2.2. Procedures. Cyclic voltammetry. An aliquot (1-10 mM) of EuCl$_3$ in suitable solvent medium (aqueous buffer medium at a desired pH in the range from pH 1-4.5; aqueous unbuffered medium or aquo-organic medium) were deaerated for at least 30 min with dry N$_2$ gas and used. Cyclic voltammograms of these solutions were recorded at HMDE/gce in the potential range between 0.0 V and −1.6 V. The experiments were recorded in single or multiple potential scan at a given scan rate between 0.005 – 50 Vs$^{-1}$. Standard methods were adopted to measure the potential and current data such as $E_{pc}$, $E_{pa}$, $E_{p/2}$, $i_{pc}$ and $i_{pa}$.

Chronopotentiometry. An aliquot (1 mM) of EuCl$_3$ in aqueous buffer medium at a desired pH in the range from pH 1-4.5 were deaerated for at least 30 min with dry N$_2$ gas. Chronopotentiogram of these solutions were recorded at HMDE at a constant current in range from 2 – 6 µA for the cathodic and 0.25 – 4.0 µA for the reverse reactions.

Chronoamperometry. An aliquot (1 mM) of EuCl$_3$ in aqueous buffer medium at a desired pH in the range from pH 1-4.5 were deaerated for at least 30 min with dry N$_2$ gas. Chronoamperograms of these solutions were recorded at HMDE at a given potential 30 mV above or below the cathodic/anodic peak potentials.

Chronocoulometry. An aliquot (1 mM) of EuCl$_3$ in aqueous buffer medium at a desired pH in the range from pH 1-4.5 were deaerated for at least 30 min with dry N$_2$ gas. Chronocoulograms of these solutions were recorded at HMDE at the potential between −0.1 to −0.8V, the cathodic/anodic peak potentials respectively.

2.2.3. Evaluation of electrochemical parameters. Cyclic Voltammetry.

(a) Rate constant and Transfer coefficient. In the electrode reaction,
where, $k_{f,h}^0$ and $k_{b,h}^0$ are the rate constants for the forward and the backward reactions\textsuperscript{29}, respectively, while Ox and Red represents the oxidized and reduced species. At the standard potential $E^0$, there is no net oxidation or reduction i.e. $E = E^0$ and hence

$$k_{f,h}^0 = k_{b,h}^0 = k_s^0$$

(2.2)

The quantity $k_s^0$ is called the standard rate constant. On the basis of absolute reaction rate theory (Butler-Volmer approach\textsuperscript{30})

$$k_{f,h}^0 = k_s^0 \exp \left[ -\alpha n_F / RT \right] [E - E^0]$$

(2.3a)

and

$$k_{b,h}^0 = k_s^0 \exp \left[ (1-\alpha) n_F / RT \right] [E - E^0]$$

(2.3b)

The parameter $\alpha$ is known as transfer coefficient.

(b) Electrochemical Reversibility. For the reaction (2.1), Nernst equation

$$E = E^0 - \left( (RT/nF) \ln \left( [\text{Red}]_0 / [\text{Ox}]_0 \right) \right)$$

(2.4)

In equation (2.4) quantities in square brackets represent the equilibrium surface concentrations of the redox species at the electrode. If E is to change isothermally to a new value $E'$, with retention of Nernstain behaviour, the surface concentration must change since all other quantities in equation (2.4) are constant. For this change to occur charge transfer has to take place at the electrode or in other word current must flow. When the charge transfer is fast (i.e $k_s^0$ is large) and/or the voltage sweep rate is relatively slow, the surface concentration remains at or very near the Nernstain values at all potentials. Under these conditions the electrode reaction is said to be reversible. When the charge transfer process is slow and/or the potential sweep rate is relatively fast, the surface concentration can no longer adjust themselves to Nernstain values. The electrode reaction is then said to be irreversible. A distinction between a quasi-reversible and a totally irreversible reaction is that, in the former case, deviation from Nernst law is not large while in the latter, the deviation is large. These definitions of electrochemical reactions are essentially operative in nature. A system may appear to be reversible under one set of conditions while it may appear to be quasi-reversible or even totally irreversible under other set of conditions.
In the above description of electrochemical reaction, effect of two parameters \( v_{0s} \) and the potential sweep rate \( (v) \) is considered. The third parameter is the rate of diffusion (i.e. the mode of mass transfer in an unstirred solution toward the stationary electrode) of Ox and Red species, back and forth to the electrode surface, because of the formation of concentration gradient. In this process the extent of observed current due to the charge transfer depends only on diffusion.

For reaction (2.1), the reversible electron transfer process for the cathodic (forward) scan, Ox is reduced thereby producing a peak. The peak arises because of the rate of variation of potential, too rapid for the diffusion process of Ox species to maintain equilibrium with the bulk of the solution. In course of cathodic variation in potential Red is produced in the vicinity of the electrode and the depletion of Ox occurs. In the mean time, Red would have diffused in to the bulk of the solution but the potential is switched back to the initial value at such a rate that Red still remained at the electrode surface and under current oxidation gives Ox. This process produces an anodic peak. One strong point of CV technique is the electrochemical characteristic of both Ox and Red one can register, starting either from Ox or Red, alone.

\( \text{(c) Reversible Charge Transfer.} \) In this case rate of charge transfer \( \gg \) potential scans rate and the current that flows is diffusion controlled. In the case of planar electrodes a situation of linear diffusion may be considered (typically of \( \sim 0.2 \text{ cm}^2 \)). In such case, the plots of cathodic current versus square root of scan rate must be linear and passing through the origin.

The theoretical treatment of i-E curves under linear diffusion was first given independently by Randles\(^{31}\) and Sevcik\(^{32}\).

\[
i = 6.02 \times 10^8 \ n^{3/2} \ A \ D_{\text{ox}} \ v^{1/2} C_{\text{ox}}^* \ (\lambda') \quad (2.5)
\]

where \( i \) is the current measured at the working electrode in \( \mu\text{A} \), \( n \) is the number of electrons, \( A \) is the area of the electrode in \( \text{cm}^2 \), \( D_{\text{ox}} \) is the diffusion coefficient of the electroactive species in \( \text{cm}^2 \text{ sec}^{-1} \) \( v \) is the scan rate in \( \text{V sec}^{-1} \) and \( C_{\text{ox}}^* \) is the bulk concentration of the electroactive species in mole liter \(^{-1} \). Values of \( \lambda' \) are a function of the applied potential (E) have been worked out and tabulated by Nicholson and Shain\(^{33}\) and Adams\(^{34}\). Some selected points of the i-E curve are as under.

\[
E \quad \quad E - E_{1/2} \ (\text{mV}) \quad \lambda'
\]
where $E_{pc}$ is the potential of the cathodic peak, $E_{1/2}$ is the polarographic half wave potential and $E_{pc/2}$ is the potential at half of the cathodic peak current. Using Eq(2.5) and the above data, the following relations are deduced for a general electrode process A more definitive treatment was later given by Nicholson and Shain.\textsuperscript{35} The current at 298K is expressed in terms of a function considering cathodic current, as

\[ i_p = 2.69 \times 10^5 \times n^{3/2} \times A \times D^{2/3} \times v^{1/2} \quad (2.6) \]

\[ E_{pc} = E_{0.5} - 28.5/n \text{ (mV)} \quad (2.7) \]

\[ E_{pc/2} = E_{0.5} + 28.5/n \text{ (mV)} \quad (2.8) \]

The peak current in a reversible process as given by Randles-Sevcik equation is

\[ i_p = k \times n^{3/2} \times A \times D^{1/2} \times C \times v^{1/2} \quad (2.9) \]

From Eq(2.7) it is seen that $E_{pc}$ is more cathodic than $E_{1/2}$. In practice the peak may be fairly broad extending over several mV and hence some times it is convenient to use $E_{pc/2}$ as a diagnostic point, although it has no direct thermodynamic significance. Finally, $E^0$ can be estimated as it occurs at a point 85.2% of the way up the wave.

The height and position of the anodic peak of the cyclic voltammogram depends on switching potential\textsuperscript{35} $E_{(ts)}$. However, if $E_{(ts)}$ is kept at $\geq 200/n$, mV more negative than $E_{pa}$ the following relations.

\[ E_{pa} = E_{1/2} + 29.5/n \quad (2.10) \]

The combination of Eq(2.8) and (2.10) yields the following conclusion.

\[ \Delta E_p = E_{pa} - E_{pc} \approx 60/n \quad (2.11) \]

Further, for a reversible process

\[ -i_{pc} = i_p \quad (2.12) \]

Eq(2.11) and (2.12) taken together, constitute the commonly used criteria of reversibility in CV. In the absence of coupled chemical reactions, continuing cycles merely gradually alter the concentration gradient near the electrode surface. The peaks slightly change shape and decrease until a steady state is achieved. The relations between the cathodic and anodic peak current and
potential is given by Matsuda. In absence of coupled chemical reactions, there is little point in going beyond the first cycle. When coupled chemical reactions are involved, marked changes may occur from cycle to cycle within the first few cycles. Under such circumstances, the first few (3 to 5) cycles are investigated. In any case containing to the steady state situation is of little interest.

(d) Quasi Reversible. (i Transfer). When the rate of charge transfer and potential scan rate become competitive, the current is controlled by both diffusion and \( k_s^0 \) and the system becomes quasi-reversible. As stated earlier, quasi-reversibility is just an initiation of irreversibility. Nernst equation is no longer applicable and absolute reaction rate equation such as equations (2.3a) and (2.3b) are used in conjunction with diffusion equations in order to obtain quantitative i- E characteristics.

The nature of i-E curves depends on three variables \( \psi, \alpha \) and \( E(t_s) \). As in the reversible case dependence of nature of i-E curves on \( E(t_s) \) can be ignored when the cathodic scan is carried sufficiently fast \( E_{pc} \). The transfer coefficient \( \alpha \), affects the symmetry of the I-E curves in two ways. For \( \alpha < 0.5 \), the cathodic peak is more rounded than the anodic peak. The broadening also results in a lowering of peak height. For \( \alpha > 0.5 \), the converse holds. The second effect is the small dependence of peak position on \( \alpha \). However, both \( E_{pc} \) and \( E_{pa} \) shift in the same direction and \( E_{pc} \) remain nearly independent of \( \alpha \) in the range 0.3 < \( \alpha \) < 0.7 (As \( \psi \) increases this approximation becomes increasingly good).

The function \( \psi \) a, dimensionless rate parameter in CV, is defined as follows:

\[
\psi = \frac{[\gamma^{\alpha} k_s]}{[\pi^{1/2} a^{1/2} D^{1/2}]} \tag{2.13}
\]

where \( \gamma \) is \( (D_o/D_R)^{1/2} \), \( \alpha \) is the electron transfer coefficient , \( k_s \) is the standard rate constant in cm/sec, \( D_o \) is the diffusion coefficient for Ox in cm\(^2\)/sec, \( D_R \) is the diffusion coefficient for Red in cm\(^2\)/sec and \( a \) is the nFv/RT sec\(^{-1} \), \( n \) is the electron transfer for electrode reaction and \( v \) is potential sweep rate (volts/sec).
When $\psi$ is large (i.e. $k_s^0$ large or small), the i-E curves can be shown to become independent of $\psi$ and $\alpha$. The system is then reversible. The limit occurs at $\psi > 7$. On the other hand, $\psi \leq 0.001$ the system is called totally irreversible and at the intermediate values of $\psi$ the system is called quasi-reversible. As $\psi$ become less than 7, both the cathodic and anodic peaks are lowered, and both waves appear drawn out i.e they occur over a wider potential range. The cathodic and anodic waves are respectively shifted cathodically and anodically. These increase the separation $\Delta E_p$ beyond 60/mV. The predicted variations of $\Delta E_p \times n$ with log $\psi$ is shown bellow.

In this table $\alpha = 0.5$. However, as long as $\psi \geq 0.5$, $\Delta E_p$ is not much sensitive to $\alpha$ within the range $0.3 < \alpha < 0.7$.

Eq(2.13) provides a reliable method for determining $k_s^0$. For this a scan rate $v$ is chosen such that $E_p \times n$ corresponds to equal to or somewhat larger than 0.5. These values of $v$ and $\psi$ in Eq(2.13). If the diffusion coefficients are known as $k_s^0$ is then immediately calculated. A simplification of Eq(2.13) is possible if $D_{Ox} = D_{Red}$. In this case $(D_{Ox}/D_{Red}) = 1$ regardless of $\alpha$.

(e) Irreversible Charge Transfer. Here $k_s^0$ is small compared to $v$. $E_{pc}$ and $E_{pa}$ are very much (several hundred mV) cathodic and anodic respectively to $E^0$. Since $E_p$ is so large $\approx 1$ V, no current observed during the reverse (anodic) scan since $E_{pa}$ may be considerably beyond the anodic sweep limit. The cathodic and the anodic processes can thus be treated completely separated.

\[
\text{Cathodic : } O_x + ne \xrightarrow{k_{c,h}^0} \text{Red} \quad \text{(2.14a)}
\]
\[
\text{Anodic : } \text{Red} \xrightarrow{k_{b,h}^0} O_x + ne \quad \text{(2.14b)}
\]

The i-E characteristics of irreversible electrode reactions have been examined theoretically by several workers. For a totally irreversible reduction occurring at a plane electrode.

\[
O_x + ne \rightarrow \text{Red} \quad \text{(2.15)}
\]
The current (at 298) for cathodic process can be expressed in terms of a current function $\lambda(b,t)$ as,

$$i = n F A C^* D^{1/2} (\alpha_{na} F/RT)^{1/2} \pi^{1/2} \lambda(b,t)$$  \hspace{1cm} (2.16)

where $\lambda(b,t)$ is a tabulated current function. The function $\lambda(b,t)$ passes through a maximum at $\pi^{1/2} \lambda(b,t) = 0.4958$. On introducing this value in Eq(2.16) the peak current expression (in amperes) obtained as,

$$i_p = 2.99 \times 10^5 \times (\alpha_{na})^{1/2} \times A \times D^{1/2} \times \nu^{1/2} \times C$$  \hspace{1cm} (2.17)

This equation can be presented in a form directly describing the peak current potential:

$$E_p = E^0 - (RT/\alpha_{na} F) \left[ 0.078 - \ln k_s + \ln \left( D_{Ox} b \right)^{1/2} \right]$$  \hspace{1cm} (2.18)

where $E^0$ is $RT/nF \ln(Ox/Red)$ known as formal potential, $b$ is the $\alpha_{na} F \nu/RT$. $E_p$ depends on parameter $b$, i.e. on the polarization rate. The dependence of $E_p$ on $\ln \nu$ is the reduction process the half wave potential becomes more negative when the polarization rate is inverse.

The half peak potential also can be used as a reference point and thus the expression becomes,

$$(E_{p/2} - E^0) \alpha_{na} + (RT/ F) \ln \left[ (\pi D_{Ox} b)^{1/2} / k_s \right] = 42.36 \text{ mV}$$  \hspace{1cm} (2.19)

$$E_p - E_{p/2} = -1.857 \text{ RT}/\alpha_{na} F \text{ at } 25^\circ \text{C}$$

$$E_{p/2} - E_p = 0.048/\alpha_{na} \text{ Volt}$$  \hspace{1cm} (2.20)

Thus for a totally irreversible wave $i_p$ is also proportional to $C^*_O$ and $\nu^{1/2}$. As $E_p$ is a function of scan rate it shifts (for a reduction) in a negative direction by an amount $30/\alpha_{na} \text{ mV}$ at 298 K for each tenfold increase in $\nu$. In this case $E_p$ occurs beyond $E^0$ by an activation over potential related to $k_0^s$. An alternative expression for $i_p$ in terms of $E_p$ can also be shown by combining Eq(2.16) and (2.19) as

$$i_p = 0.227 \times (n F A C^*_O \times D^{1/2} \times k_0^s) \exp[ - (\alpha_{na} F/RT) (E_p - E^0) ]$$  \hspace{1cm} (2.21)

A plot of $i_p$ vs $(E_p - E^0)$, assuming $E^0$ could be obtained, determined at different scan rates should have a slope of $-\alpha_{na} F/RT$ and an intercept proportional to $k_s^0$. The values of kinetic parameters (viz. $k_0^s$, $\alpha_{na}$) can be also be obtained by the method developed by Reinmuth. According to this method the currents on the plateau are related to the potential ($E$) and the initial potential ($E_i$) as given by equation
Chapter 2

Electrochemistry of Eu(III)

\[ i = n F A C_0 \ast k^0 \exp [-(\alpha_{nF}/RT) (E - E_i)] \]  

(2.22)

Eq (2.18) can be transformed into the expression,

\[ E_p = -1.14 \frac{(RT/\alpha_{nF}) + (RT/\alpha_{nF}) \ln (k^0_{f,h}/D^{1/2} - [(RT/2\alpha_{nF})\ln \alpha_{nF}] \nu)}{(2.23)} \]

Where \( k^0_{f,h} \) is the heterogeneous rate constant for forward reduction at \( E=0 \) on potential scale in use (cm/sec).

(f) Electrode process followed by first order Reaction. Consider a simple reversible electron transfer reaction coupled to a chemical reaction as

\[ \text{Ox} + \text{ne} \rightleftharpoons \text{Red} \]  

(2.24a)

\[ \text{Red} \rightleftharpoons \text{X} \]  

(2.24b)

In this case the product of the electrode reaction, Red, reacts to produce a species that is not electro active at potentials where the reduction of Ox is occurring. The potential of the current peak is expressed by the eq (2.25).

\[ E_p = E_{1/2} - \frac{(RT/nF)}{0.78 + \ln K (a/l)\nu^{1/2} - \ln (1+K)} \]  

(2.25)

where \( K \) is chemical equilibrium constant for the chemical reaction and \( l \) is the sum of the rate constants \( (k_r + k_b) \). or taking in to account the components of \( a \),

\[ E_p = E_{1/2} - \frac{(RT/nF)}{0.78 + [(RT/2nF) \ln (RT/nF)] + [(RT/2nF) \ln k_1/\nu]} \]  

(2.26)

(g) Effect of pH on peak potentials. In case of protons involvement in the electrode process, the peak potential will depend on the concentrations of protons i.e, on pH. To delineate its quantitative aspects it is necessary to examine the value of \( E_{0.5} \) which is usually called polarographic half-wave potential. For the Nerstain case.

We have

\[ E = -(RT/nF) \ln [\text{Red}]_0/[	ext{Ox}]_0 \]  

(2.27)

Eq(2.27) can be readily transform to

\[ E_{0.5} = E_T^{0'} - (RT/nF) \ln (D_{\text{Ox}}/D_{\text{Red}})\nu^{1/2} \]  

(2.28)

Where \( E_T^{0'} \) is the formal electrode potential and the other symbols have their usual meanings.

Consider the electrode reaction in which protons are also involved

\[ \text{Ox} + \text{ne} + m\text{H}^+ \rightleftharpoons \text{Red.} \]  

(2.29)

The Nernstain equation for above reaction is
\[ E_{0.5} = E_T^0 \cdot -\frac{RT}{nF} \ln \frac{[\text{Red}]_0}{[\text{Ox}]_0} \cdot \frac{[\text{H}^+]}{[\text{H}^+]} \]  

(2.30)

The quantity \([\text{H}^+]\) i.e., the concentration of protons at the electrode surface is in general current dependent since \(\text{H}^+\) is component of the electrode reaction. In case when the solution is well buffered and having enough buffer capacity, the \([\text{H}^+]_0\) will remain virtually constant and will be equal to \([\text{H}^+]\), i.e., the bulk concentration. Under these condition Eq(2.30) can be written as,

\[ E_{0.5} = E_T^0 \cdot -\frac{RT}{nF} \ln \frac{[\text{Red}]_0}{[\text{Ox}]_0} + (mRT/nF) \ln [\text{H}^+]_0 \]  

(2.31)

And at 298 K it reduce to

\[ E = E_{298}^0 \cdot -(0.059/n) \log \frac{[\text{Red}]_0}{[\text{Ox}]_0} - 0.059 \left( \frac{m}{n} \right) \text{pH} \]  

(2.32)

Reconsidering Eq(2.27)and (2.28), it is evident that Eq(2.32), can be written as,

\[ E_{0.5} (\text{H}^+) = E_{298}^0 \cdot -(0.059/n) \log \frac{[\text{Dox}]}{[\text{Dred}]} - 0.059 \left( \frac{m}{n} \right) \text{pH} \]  

(2.33)

where, \(E_{0.5} \text{H}^+\) represents half wave potential for reaction (2.29) involving protons. In the usual assumption \(\text{Dox} \approx \text{Dred}\) is made equation reduce to,

\[ E_{0.5} (\text{H}^+) = E_{298}^0 \cdot -(0.059/n) \left( \frac{m}{n} \right) \text{pH} \]  

(2.34)

and the two peak potential equations for the reversible reaction (2.29) are,

\[ E_{pc} = E_{0.5} (\text{H}^+) -28.5/n \text{ mV} \]  

(2.35)

\[ E_{pa} = E_{0.5} (\text{H}^+) +29.5/n \text{ mV} \]  

(2.36)

On combining Eq(2.35) and (2.36) one gets

\[ 0.5 \left( E_{pc} + E_{pa} \right) = E_{0.5} (\text{H}^+) + 0.5/n \text{ mV} \]  

(2.37)

substituting (2.37) in to (2.34) and noting that the quantity 0.5/n mV is negligible since it is much smaller than the accuracy 5-10 mV with which peak potentials can be located, one writes the useful equation.

\[ E_{298}^0 = E_p + (0.059) \left( \frac{m}{n} \right) \text{pH} \]  

(2.38)

where \(E_p = E_{pc} - E_{pa}\) eq (2.38) provides a powerful method for determination of \(E_{298}^0\), from cyclic voltammogram in buffered media.

**Chronopotentiometry.** Consider a simple reversible electron transfer reaction

\[ \text{Ox} + n\text{e} \quad \text{Red} \]  

(2.39)
diffusion Eq(2.40) and (2.41) and the boundary conditions (2.42) are applied to Eq(2.39) and the resulting equation (2.42) is given below.

\[
dC_O(x,t) / dt = D_O [d^2 C_O(x, t) / dx^2] \quad (2.40)
\]
\[
dC_R(x,t) / dt = D_R [d^2 C_R(x, t) / dx^2] \quad (2.41)
\]

At \( t = 0 \) and \( x \) and at \( t \geq 0 \) and \( x = \infty \) \( (2.42) \)

and

\[
D_O [dC_O(x,t) / dx]_{x=0} + D_R [d C_R(x, t)/ dx]_{x=0} = 0 \quad (2.43)
\]

Further the flux at the electrode surface at any time \( t \) and at any applied current \( i \) is given as

\[
D_O [dC_O(x,t) / dx]_{x=0} = i(t) / nFA \quad (2.44)
\]

On applying Laplace transform method\(^1\) to (2.41) and (2.42) yields.

\[
C_O(x,s) = (C^*_O / s) + B(s) \exp. [- (s/D_O)^{1/2} x] \quad (2.45)
\]

And the transform of (2.44) is

\[
D_O [dC_O(x,s) / dx]_{x=0} = i(t) / nFA \quad (2.46)
\]

The combination of (2.45) and (2.46) with elimination of the integration constant \( B(s) \) finally yields

\[
C_O(x,s) = (C^*_O / s) + B(s) - [i(s) / nFA D_O^{1/2} s^{1/2}] \exp. [- (s/D_O)^{1/2} x] \quad (2.47)
\]

\([dC_O(x,t)/dx]_{x=0}\) is constant at all times after the onset of electrolysis and \( C_O(x,t) \) decrease continuously. An expression for \( C_O(0,t) \) can be obtained by setting \( x=0 \) in Eq(2.47)

By substitution of the known function, \( i(s) \), and employing the inverse transform, \( C_O(x,s) \) can be obtained.

If \( i(t) = i \) (constant), then \( i(s) = i/s \) and equation (2.48) becomes,

\[
C_O(x,s) = (C^*_O / s) - [i(s) / nFA D_O^{1/2} s^{3/2}] \exp. [- (s/D_O)^{1/2} x] \quad (2.48)
\]

At certain characteristic time \( \tau \), called transition time, \( C_O(0,t) \) drops to zero. At this time \( i \)

\[
| i \tau^{1/2} | = \frac{(nF D_o^{1/2} \pi^{1/2} C_o^{\infty})}{2} \quad (2.49)
\]

This equation known as the Sand equation\(^1\).

For the rapid electron transfer, the Nernst equation applies substitution of the expressions for \( C_O(0, t) \) and \( C_R(0, t) \) in to it yields

\[
E = E_{\tau/4} + RT/NF \ln (\tau^{1/2} - t^{1/2}/t^{1/2}) \quad (2.50)
\]
where $\tau$ is the transition time, thus the product $i\tau^{1/2}$ is independent of the applied current density and proportional to $C_0^{-x}$. This is used as a diagnostic test for diffusion controlled process. Where $E_{1/4}$ is the quarter wave potential,

$$E_{1/4} = E^0 - \frac{RT}{NF} \ln \left(\frac{D_o}{D_R}\right)$$

(2.51)

So that $E_{1/4}$, is the chronopotentiometric equivalent of the voltammetric $E_{1/2}$ value. In case of reversible reactions, the plot $E$ vs log \( [\tau^{1/2} - t^{1/2} / t^{1/2}] \) is linear with a slope $= 0.059/n$ V and $|E_{1/4} - E_{3/4}| = 47.9/n$ mV at (25°C).

In case of quasi reversible reactions, the plot of $\eta$ vs $t^{1/2}$

$$-\eta = (RT/nF) i \left[2t^{1/2} / nFAD^{1/2} \left(1/C_o^{x} \right) + \frac{1}{1/2^n} \right]$$

(2.52)

In case of irreversible reactions,

$$E = (RT/\alpha_nF) \ln \left[2k^0 / (\pi D_o)^{1/2} \right] + (RT/\alpha_nF) \ln \left(\tau^{1/2} - t^{1/2} \right)$$

$$E = E^0 + (RT/\alpha_nF) \ln \left[2k^0 / (\pi D_o)^{1/2} \right] + (RT/\alpha_nF) \ln \left(\tau^{1/2} - t^{1/2} \right)$$

(2.53a)

Thus, for a totally irreversible reduction wave the whole E-t wave shifts toward more negative potentials with increase in current,[ with a tenfold increase in current causing a shift of 2.3RT/\alpha_nF(or 59/\alpha_n mV at 25°C)]. For a totally irreversible wave, $|E_{1/4} - E_{3/4}| = 33.8 /\alpha_n$ mV at 25°C.

**Chronoamperometry.** Current-time response is expressed using the Cottrell equation\(^{42}\). The plots of $it^{1/2}$ vs $t$ is linear. The values of diffusion coefficient of $Ox$ can be evaluated from the following equation

$$\left|i \right| = \frac{(nFAD^{1/2}C^{x})}{(\pi^{1/2} t^{1/2})}$$

(2.54)

where $n$ is number of electrons transferred in the electrolysis, $F$ is Faraday's constant (96,500 C mol\(^{-1}\)), $A$ is electrode area (cm\(^2\)), $C$ is a concentration in milli moles and $D$ is diffusion coefficient (cm\(^2\) s\(^{-1}\)).

**Chronocoulometry.** The plots of $it^{1/2}$ vs $t$ are linear. The values of diffusion coefficient of $Ox$ is calculated according to the integration of the Cottrell equation:

$$\left|Q \right| = \frac{(2n FAD^{1/2}C^{x} t^{1/2})}{\pi^{1/2}}$$

(2.55)

where $C^{x}$ is concentration (milli moles), $Q$ is the instantaneous charge in coulombs, $t$ is the time in seconds , $n$ is the number of electrons transferred per molecule, $F$ is Faraday's constant.
(96,500 C mol$^{-1}$), A is electrode area (cm$^2$), D is diffusion coefficient (cm$^2$ s$^{-1}$) and C$\propto$ is a concentration (mol cm$^{-3}$).

2.2.4. Instrumentation. All electrochemical measurements like cyclic voltammetry, chronopotentiometry, chronoamperometry and chronocoulometry were conducted on CHI-600Asp electrochemical analyzer in conjunction with EG$\&$G PARC model 384B Polarographic Analyzer, preloaded with CHI software program. A three electrode cell assembly EG$\&$G PARC 303A(SMDE/HMDE/DME) was used. A hanging mercury drop electrode (HMDE) of area 0.016 cm$^2$ or glassy carbon electrode (gce) of area 0.008 cm$^2$ as working, Ag/AgCl in 3 M NaCl as reference and a platinum wire as a counter electrode were used. All the experiments were conducted in a double walled cell maintained at 25 ± 0.1 °C.

Orion Ion analyzer model 940 equipped with combined glass electrode was used to measure pH within ± 0.01.

2.3 Results and Discussion.

Cyclic voltammetric behaviour of Eu(III)/Eu(II) couple has been investigated in three different medium viz. aqueous buffered, aqueous unbuffered and aquo-organic. The study is performed at a wide range of potential sweep rates from 0.005V s$^{-1}$ to 100 V s$^{-1}$ categorized into three ranges named as slow (≤ 0.050 V s$^{-1}$), moderate, (≤ 0.90 V s$^{-1}$) and high (1-100 V s$^{-1}$). For thorough understanding of the system, the effect of different experimental variables like pH, Eu(III) concentration, supporting electrolyte and solvent medium has been investigated systematically. Further, the Eu(III)/Eu(II) couple has been investigated by chrono techniques viz chronopotentiometry, chronoamperometry and chronocoulometry to obtain additional information in support to cyclic voltammetry.

2.3.1. Cyclic voltammetric behaviour of Eu(III)/Eu(II) couple in aqueous buffered medium. The cyclic voltammetric behaviour of Eu(III)/Eu(II) couple is investigated in the aqueous buffer (NaCl-HCl; NaOAc-HCl, Na$_2$SO$_4$-H$_2$SO$_4$; NaOAc-H$_2$SO$_4$) medium at a desired pH by varying scan rates between 0.005-100 V s$^{-1}$ in the potential range of 0.0 to −1.6 V vs Ag/AgCl.

Cyclic voltammetry in NaCl-HCl medium. Cyclic voltammetric responses observed at a HMDE for 1.0 mM EuCl$_3$ in 0.1 N NaCl-HCl medium at pH values 1.0 and 2.5 are shown at
four different scan rates in all ranges, slow (≤ 0.050 V s⁻¹), moderate (≤ 1.0 V s⁻¹) and high (1-100 V s⁻¹).

**pH 2.5.**

*Slow scan rate.* At scan rate of 0.01 V s⁻¹, Eu(III) exhibited a single cathodic peak at −0.655 V in the forward scan and the corresponding anodic peak at −0.565 V in the reverse scan as seen in Figure 2.1(a). The $E_{p/2} - E_p$ value obtained from the cathodic peak is 54 mV, which confirmed the reduction process as one electron step. The peak separation is 90 mV while the anodic to cathodic peak current ratio is 0.9, indicating that the electrode process is quasi reversible. Similar response is seen at other scan rates 0.02, 0.03 and 0.05 V s⁻¹ [Figure 2.1(b-d)]. The cyclic voltammetric data are given in Table 2.3. It can be seen that the cathodic and anodic peak potential and the peak separation ($\Delta E_p$) varied slightly with increase in sweep rate. Also, the $E_{p/2} - E_p$ value for the cathodic response is almost steady at 52 mV. However, the peak current ratio ($i_{pa}/i_{pc}$) is decreased with the increase in scan rate and a new anodic peak ($E_{a2}$) is appeared in the potential range −0.30 to −0.35 V at scan rates 0.03 and 0.05 V s⁻¹. This indicates that a chemical reaction is associated to the electrochemical reduction of Eu(III), which is discussed in the later part of this section. The $E_{1/2}$ value (vs. Ag/AgCl) for the Eu (III)/Eu (II) couple as estimated from $(E_{pc} + E_{pa})/2$ is 0.612 V which is very close to the literature value of −0.674 V.
The plots of $i_{pc}$ and $i_{pa}$ vs square root of scan rate $v^{1/2}$ are found linear and passing through the origin. Plot 2.1(a, b) indicates diffusion controlled processes for the forward and backward electrode reaction.

### Table 2.3. Cyclic voltammetric data of Eu(III)/Eu(II) couple in 0.1N NaCl-HCl at pH 2.5 at 25 °C.

<table>
<thead>
<tr>
<th>Scan rate V s⁻¹</th>
<th>$-E_{pc}$ V</th>
<th>$-E_{pa}$ V</th>
<th>$\Delta E_p$ mV</th>
<th>$i_{pa}/i_{pc}$</th>
<th>$E_{p2}-E_p$ V</th>
<th>$-E_{1/2}$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.655</td>
<td>0.565</td>
<td>90</td>
<td>0.85</td>
<td>0.54</td>
<td>0.610</td>
</tr>
<tr>
<td>0.02</td>
<td>0.656</td>
<td>0.564</td>
<td>92</td>
<td>0.77</td>
<td>0.52</td>
<td>0.610</td>
</tr>
<tr>
<td>0.03</td>
<td>0.658</td>
<td>0.565</td>
<td>93</td>
<td>0.72</td>
<td>0.52</td>
<td>0.611</td>
</tr>
<tr>
<td>0.05</td>
<td>0.663</td>
<td>0.565</td>
<td>98</td>
<td>0.67</td>
<td>0.52</td>
<td>0.614</td>
</tr>
</tbody>
</table>

**Effect of Eu(III) concentration.** The cyclic voltammetric responses of 1mM, 2mM, 3mM and 5mM Eu(III) are also studied in scan rate range 0.01-0.05 V s⁻¹. Representative data at 0.02V s⁻¹ are shown in Figure 2.2. The peak current ($i_{pc}$ and $i_{pa}$) data at a given scan rate is increased linearly with the increase in Eu(III) concentration with a negligible change in peak potentials. $i_{pc}$ and $i_{pa}$ vs concentration of Eu(III) are shown in plot 2.2 (a, b) respectively. This indicate the diffusion controlled nature of Eu(III)/Eu(II) couple system.

**Moderate scan rate.** The cyclic voltammetric responses of Eu(III) at moderate scan speeds are shown in Figure 2.3(a-d). At 0.08 V s⁻¹, the solution exhibited a single cathodic peak at −0.662 V in the forward scan and two anodic peaks $E_{a1}$ and $E_{a2}$ at potential −0.562 V and −0.318 V respectively. The cathodic response is sharp and shifted cathodically with the...
increase in scan rate. The $E_{p/2} - E_p$ value for the cathodic response is 53 mV at 0.08 V s$^{-1}$ and increased to 61 mV at 0.9 V s$^{-1}$. On the other hand, the anodic peaks $E_{a1}$ and $E_{a2}$ are broad and the peak separation ($\Delta E_p$) is 100 mV with respect to $E_{a1}$ and 344 mV with respect to $E_{a2}$. In all repetitive cycles, the single cathodic peak and the two anodic peaks (peaks $E_{a1}$ and $E_{a2}$) are obtained. The formation of new cathodic response as the counter part of peak $E_{a2}$ is not noticed, indicate that the anodic reactions at Peaks $E_{a1}$ and $E_{a2}$, represent the oxidation of two different species of Eu(II) coupled through a chemical step, are the counter part of the single cathodic reaction at $-0.662$ V. The plot of cathodic peak current vs square root of scan rate, [Plot 2.3(a, b and c)] is linear and passed through origin, which confirmed the diffusion controlled reduction of Eu(III).

Similarly, the anodic peaks (Peak $E_{a1}$ and $E_{a2}$), shows linear relationships with the square root of scan rates confirm the diffusion-controlled nature of the oxidation peaks $E_{a1}$ and $E_{a2}$. The position of peak $E_{a1}$ remained unchanged while that of peak $E_{a2}$ shifted steadily to positive potentials. The CV data for the reduction of Eu(III) at moderate scan rates are summarized in Table 2.4. The $E_{p/2} - E_p$ value are lying in the range from 53-61 mV while the values of $\Delta E_{p1}$ ($E_{pc} - E_{pa1}$) and $\Delta E_{p2}$ ($E_{pc} - E_{pa2}$) varied between 100-140 and 340-470 mV, respectively depending on the scan rate. The current ratio, $i_{pa1}/i_{pc}$ and $i_{pa2}/i_{pc}$ for both the anodic peaks are less than one. Interestingly, the ratio, $i_{pa1}/i_{pc}$ is greater than that of $i_{pa2}/i_{pc}$ at a given scan rate. However, the ratio $i_{pa1}/i_{pc}$ is decreased with the increase in scan rate while that of $i_{pa2}/i_{pc}$ increased concomitantly with increase in scan rate. The oxidation peak is more predominantly
seen at slow scan rates whereas the peak $E_{a2}$ is more predominant at higher scan rates. This explains the rapid formation of Eu(II) by the reduction of Eu(III) species and its spontaneous transformation to another form of stable Eu(II) species through a chemical step which is discussed later.

**Table 2.4.** Cyclic Voltammetric data of Eu(III)/Eu(II) couple in 0.1N NaCl-HCl medium at pH 2.5, at 25 °C.

<table>
<thead>
<tr>
<th>Scan rate V s$^{-1}$</th>
<th>$-E_{pc}$ V</th>
<th>$-E_{pa1}$ V</th>
<th>$-E_{pa2}$ V</th>
<th>$\Delta E_{p1}$ mV</th>
<th>$\Delta E_{p2}$ mV</th>
<th>$i_{pa1}/i_{pc}$</th>
<th>$i_{pa2}/i_{pc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08</td>
<td>0.662</td>
<td>0.562</td>
<td>-0.318</td>
<td>100</td>
<td>344</td>
<td>0.64</td>
<td>0.03</td>
</tr>
<tr>
<td>0.20</td>
<td>0.674</td>
<td>0.562</td>
<td>-0.277</td>
<td>112</td>
<td>397</td>
<td>0.53</td>
<td>0.10</td>
</tr>
<tr>
<td>0.50</td>
<td>0.694</td>
<td>0.561</td>
<td>-0.248</td>
<td>133</td>
<td>446</td>
<td>0.47</td>
<td>0.20</td>
</tr>
<tr>
<td>0.90</td>
<td>0.702</td>
<td>0.563</td>
<td>-0.234</td>
<td>139</td>
<td>468</td>
<td>0.42</td>
<td>0.24</td>
</tr>
</tbody>
</table>

**Effect of Eu(III) concentration.** The cyclic voltammetric responses of 1mM, 2mM, 3mM and 5mM Eu (III) were also studied in this scan rate range. Representative data at 0.5 V s$^{-1}$ are shown in Figure 2.4. The cathodic peak potentials is found shifted cathodically with respect to increase in concentration whereas the anodic peak potentials $E_{a2}$ remained almost constant but an anodic shift is observed in case of $E_{a1}$. The peak current of the cathodic ($i_{pc}$) and those of anodic peaks $E_{p1}$ and $E_{p2}$, are increased linearly with the increase in Eu(III) concentration. Plots of $i_{pc}$, $i_{pa1}$, and $i_{pa2}$ vs concentration of Eu(III) are shown in [Plot 2.4 (a-c)]. This indicated the diffusion controlled nature of the single reduction and the two anodic processes of Eu(III)/Eu(II) couple.
High scan speeds. The cyclic voltammetric responses of Eu(III)/(Eu(II) couple at higher scan rates (1 – 100 V s⁻¹) are shown in Figure 2.5. At 10 V s⁻¹, Eu(III) exhibited a sharp cathodic peak at –0.775 V in forward scan and an anodic peak E_a2 at –0.148 V in the reverse scan, [Figure 2.5(a)]. Here, no anodic peak representing the anodic peak E_a1 is found at these scan rates. The E_p/2 – E_p value for the cathodic response is 72 mV. The peak separation is found 627 mV while the anodic to cathodic peak current ratio is 0.5, indicates the irreversible nature of the electrode process. The cyclic voltammograms showed an increase in peak height with increase in scan rate. The peak intensity of both the cathodic and anodic responses increased with increase in scan rate. The [plot-2.5 (a-b)] of i_p vs square root of scan rate v¹/² is linear and passed through the origin. This ascertained the diffusion controlled nature of the electrode process.

Table 2.5. Cyclic voltammetric data of Eu(III)/Eu(II) couple in 0.1N NaCl-HCl medium at pH 2.5 at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s⁻¹</th>
<th>–E_p V</th>
<th>–E_p a V</th>
<th>ΔE_p mV</th>
<th>i_pa / i_pc</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.775</td>
<td>0.148</td>
<td>627</td>
<td>0.487</td>
</tr>
<tr>
<td>20</td>
<td>0.794</td>
<td>0.125</td>
<td>669</td>
<td>0.525</td>
</tr>
<tr>
<td>50</td>
<td>0.852</td>
<td>0.062</td>
<td>790</td>
<td>0.456</td>
</tr>
</tbody>
</table>

The data in Table 2.5 indicate the peak separation is increased with increase in scan rate. Similarly, the E_p/2 – E_p value for the cathodic response is 69-82 mV. The ratio of i_pa/i_pc is found varied from 0.45 to 0.52.
Effect of Eu(III) concentration. The cyclic voltammetric responses of 1mM, 2mM, 3mM and 5mM Eu (III) are also studied in this scan rate range. Representative data at 25 V s$^{-1}$ are shown in Figure 2.6. The values of the $i_{pc}$ and $i_{pa}$ are increased linearly with the increase in Eu(III) concentration with a cathodic shift in peak positions. The nature of $i_{pc}$ and $i_{pa}$ vs concentration of Eu(III) is shown in plot 2.6 respectively. This indicated the diffusion controlled nature of Eu(III)/Eu(II) couple processes.

pH 1.0.

Slow scan rate. The cyclic voltammetric responses of the Eu(III) at slow scan rates (0.005, 0.01, 0.02 and 0.03 Vs$^{-1}$) are shown in Figure 2.7. The cyclic voltammogram at 0.005 V s$^{-1}$ showed a single cathodic peak in the forward scan and a single anodic peak in the reverse scan at $-0.705$ V and $-0.675$ V, respectively is shown in Figure 2.7(a). The $E_{p/2}$–$E_p$ value for the cathodic response is 66 mV,
which confirmed the reduction process as one electron step. The peak separation is 30 mV while the anodic to cathodic peak current ratio is 0.69, which is less than one, indicating that the electrode process is nearly reversible as found at pH 2.5. However, the ratio, $i_{pa}/i_{pc}$ decreased with the increase in scan rate. The $E_{1/2}$ value for the Eu(III)/Eu(II) couple as estimated from $(E_{pc}+E_{pa})/2$ is $-0.689$ V vs Ag/AgCl which is 77 mV more negative than that observed at pH 2.5.

Table 2.6. Cyclic voltammetric data of Eu(III)/Eu(II) couple in 0.1N NaCl-HCl medium at pH 1.0 at 25 °C.

<table>
<thead>
<tr>
<th>Scan rate V s$^{-1}$</th>
<th>$-E_{pc}$ V</th>
<th>$-E_{pa}$ V</th>
<th>$\Delta E_p$ mV</th>
<th>$i_{pa}/i_{pc}$</th>
<th>$-E_{1/2}$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>0.705</td>
<td>0.675</td>
<td>30</td>
<td>0.73</td>
<td>0.69</td>
</tr>
<tr>
<td>0.01</td>
<td>0.720</td>
<td>0.650</td>
<td>70</td>
<td>0.59</td>
<td>0.68</td>
</tr>
<tr>
<td>0.02</td>
<td>0.732</td>
<td>0.606</td>
<td>126</td>
<td>0.48</td>
<td>0.67</td>
</tr>
<tr>
<td>0.03</td>
<td>0.732</td>
<td>0.626</td>
<td>106</td>
<td>0.53</td>
<td>0.68</td>
</tr>
</tbody>
</table>

The values of $i_{pc}$ and $i_{pa}$ vs square root of scan speed ($v^{1/2}$) is linear and passing through origin as shown in Plot 2.7(a, b). This indicates that the electrode processes (cathodic and anodic) are under diffusion controlled.

Moderate scan rate. The cyclic voltammograms of Eu(III) recorded at moderate scan rates are shown in Figure 2.8. The solution exhibited a single cathodic peak ($-0.736$ V at 0.1 V s$^{-1}$) in the forward scan. The cathodic response observed is sharp and shifted cathodically with the increase in scan rate. The $E_{p/2}$ value for the cathodic response is found to be 61 mV at 0.1 V s$^{-1}$ and increases to 65 mV with increase in scan rate (Table 2.7). On the other hand, the anodic peak is

![Plot 2.8. Plot of $i_p$ vs square root of scan rate](image)

![Figure 2.8. Cyclic voltammetric responses of 1 mM Eu(III) in 0.1 N NaCl-HCl medium at pH 1.0 at scan rates (a) 0.1;(b) 0.2; (c) 0.50; (d) 0.7; (e) 0.9 V s$^{-1}$. Temperature of the solution is 25 °C.](image)
observed diffusive in nature and shifted anodically with increase in scan speed. Unlike at pH 2.5, a single anodic peak (−0.419 V at 0.1 V s⁻¹) is observed in the reverse scan at potential very close to the potential of peak 2 as shown in Figure 2.5. The peak separation (ΔEₚ) is from 317 mV to 382 mV indicating the Eu(III)/Eu(II) couple, totally irreversible in nature. However, the cathodic and the anodic peaks are observed repeatedly in all subsequent cycle shows the complex behavior of the europium ion.

The plot of cathodic peak current vs square root of scan rate, [Plot 2.8 (a, b)] is linear and passed through origin which confirmed the diffusion controlled reduction of Eu(III) at Hg-electrode at moderate scan speeds. Similarly, the anodic peak is increasing linearly with the increase in square root of scan rate confirm the diffusion-controlled behaviour of the anodic response.

Table 2.7. Cyclic voltammetric data of Eu(III)/Eu(II) couple in 0.1N NaCl-HCl medium at pH 1.0 at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s⁻¹</th>
<th>−Eₚc V</th>
<th>−Eₚa₁ V</th>
<th>ΔEₚ mV</th>
<th>iₚc μA</th>
<th>iₚa μA</th>
<th>iₚa/iₚc</th>
<th>Eₚa²-Eₚc mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.736</td>
<td>0.419</td>
<td>317</td>
<td>3.59</td>
<td>0.30</td>
<td>0.08</td>
<td>61</td>
</tr>
<tr>
<td>0.2</td>
<td>0.753</td>
<td>0.385</td>
<td>368</td>
<td>5.04</td>
<td>0.72</td>
<td>0.14</td>
<td>61</td>
</tr>
<tr>
<td>0.5</td>
<td>0.759</td>
<td>0.379</td>
<td>380</td>
<td>7.99</td>
<td>1.39</td>
<td>0.17</td>
<td>64</td>
</tr>
<tr>
<td>0.7</td>
<td>0.762</td>
<td>0.380</td>
<td>382</td>
<td>9.30</td>
<td>1.85</td>
<td>0.20</td>
<td>63</td>
</tr>
<tr>
<td>0.9</td>
<td>0.774</td>
<td>0.360</td>
<td>353</td>
<td>10.64</td>
<td>2.90</td>
<td>0.27</td>
<td>65</td>
</tr>
</tbody>
</table>

*High scan rate.* The cyclic voltammetric response of Eu(III) recorded at higher scan rates (1 − 100 V s⁻¹) are shown in Figure 2.9. At 10 V s⁻¹, the Eu(III) exhibited a sharp cathodic peak at −0.819 V in forward scan and a corresponding anodic peak at −0.307 V in the reverse scan. The Eₚa²−Eₚ value for the cathodic response is 70 mV, the peak separation of 512 mV and the peak current

![Plot 2.9. Plot of iₚ vs square root of scan rate](image_url)
ratio less than 0.5, indicating the irreversible nature of the electrode process. The cyclic voltammograms recorded at other scan rates

Figure 2.9(b-d), showed an increase in peak separation with increase in scan rate. The peak intensity of both the cathodic and anodic responses are increased with the increase in scan speed. The plots of $i_{pc}$ and $i_{pa}$ vs square root of scan rates ($v^{1/2}$) is linear and passed through the origin [Plot 2.9(a, b)]. This indicate the reduction and the subsequent oxidation process of Eu(III) is diffusion controlled.

**Table 2.8.** Cyclic voltammetric data of Eu(III)/Eu(II) couple in 0.1N NaCl-HCl medium at pH 1.0 at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s$^{-1}$</th>
<th>$-E_{pc}$ V</th>
<th>$-E_{pa}$ V</th>
<th>$\Delta E_p$ mV</th>
<th>$i_{pc}$ µA</th>
<th>$i_{pa}$ µA</th>
<th>$i_{pa}/i_{pc}$</th>
<th>$E_{p2}-E_{p}$ mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.819</td>
<td>0.307</td>
<td>512</td>
<td>32.85</td>
<td>13.33</td>
<td>0.41</td>
<td>70</td>
</tr>
<tr>
<td>20</td>
<td>0.829</td>
<td>0.294</td>
<td>535</td>
<td>47.68</td>
<td>20.48</td>
<td>0.43</td>
<td>77</td>
</tr>
<tr>
<td>25</td>
<td>0.841</td>
<td>0.279</td>
<td>562</td>
<td>52.85</td>
<td>23.31</td>
<td>0.44</td>
<td>75</td>
</tr>
<tr>
<td>50</td>
<td>0.860</td>
<td>0.255</td>
<td>605</td>
<td>71.54</td>
<td>32.59</td>
<td>0.46</td>
<td>80</td>
</tr>
</tbody>
</table>

The data in Table 2.8 shows that the peak separation $\Delta E_p$ is increasing with increase in scan rate. Similarly, the $E_{p2}-E_{p}$ value for the cathodic response is 70-80 mV and the ratio of $i_{pa}/i_{pc}$ is 0.41 at 10 V s$^{-1}$ and observed increased slightly with increase in scan rate due to its diffusive nature.

**pH 4.5.**

The electrochemical behavior of Eu(III) at pH 4.5 is studied in 0.2 N CH$_3$COONa -HCl media. Cyclic voltammetric responses of 0.1 mM Eu(III) are recorded at three different range of scan rates viz. slow ($\leq$ 0.050 V s$^{-1}$), moderate ($\leq$ 1.0 V s$^{-1}$) and high (1-100 V s$^{-1}$) and the data are presented in Figures 2.10-2.13, respectively.

**Slow scan rates.** Cyclic voltammetric responses of Eu(III) ion recorded at four different scan rates (0.01, 0.02, 0.03 and 0.05 V s$^{-1}$) are
shown in Figure 2.10, At 0.01 V s\(^{-1}\), the solution exhibited a single cathodic peak at \(-0.747\) V in forward scan and a single anodic peak at \(-0.645\) V in reverse scan [Figure 2.10(a)]. The \(E_{p/2} - E_p\) value for the cathodic response is 67 mV, which ascertained the reduction process as one electron step. The cathodic and anodic peaks are separated by 100 mV which is more than the theoretical value (i.e. 60 mV) while the anodic to cathodic peak current ratio of 0.92, which is less than one, indicate the electrode process is nearly reversible at these scan rates. The data in Table 2.9 and Figure 2.10(a-d) indicate that with increase in scan speed, the cathodic peak shifted to negative potentials while the anodic peak to positive potentials. As a result, the \(\Delta E_p\) value increased steadily to 180 mV and the peak current ratio \((i_{pa}/i_{pc})\) decreased with the increase in scan rate. However, the \(E_{p/2} - E_p\) value for the cathodic response is almost unchanged.

<table>
<thead>
<tr>
<th>Scan rate (V\ s^{-1})</th>
<th>(-E_{pc}) V</th>
<th>(-E_{pa}) V</th>
<th>(\Delta E_p) mV</th>
<th>(i_{pc}) (\mu)A</th>
<th>(i_{pa}) (\mu)A</th>
<th>(i_{pa}/i_{pc})</th>
<th>(E_{p/2} - E_p) mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.747</td>
<td>0.645</td>
<td>102</td>
<td>1.58</td>
<td>1.46</td>
<td>0.92</td>
<td>67</td>
</tr>
<tr>
<td>0.02</td>
<td>0.765</td>
<td>0.626</td>
<td>139</td>
<td>2.14</td>
<td>2.00</td>
<td>0.94</td>
<td>70</td>
</tr>
<tr>
<td>0.03</td>
<td>0.772</td>
<td>0.621</td>
<td>158</td>
<td>2.66</td>
<td>2.15</td>
<td>0.81</td>
<td>72</td>
</tr>
<tr>
<td>0.05</td>
<td>0.778</td>
<td>0.598</td>
<td>180</td>
<td>3.15</td>
<td>2.18</td>
<td>0.69</td>
<td>69</td>
</tr>
</tbody>
</table>

The peak intensities of both the cathodic and anodic responses is increased with the increase in scan rate. The plots of \(i_{pc}\) and \(i_{pa}\) vs square root of scan speed is linear and passing through origin [Plot 2.10(a, b)]. This indicates that the cathodic and anodic processes are diffusion controlled.

*Moderate scan rates.* The cyclic voltammograms of EuCl\(_3\) solution recorded at moderate scan speeds are shown in Figure 2.11. The solution exhibited a single cathodic peak in forward scan and a single anodic peak in the reverse scan. The cathodic response is sharp and shifted cathodically with the increase in scan speed. On the other hand, the anodic peak was broad and diffusive in nature. The difference in \(E_{p/2} - E_p\) value for the cathodic response is 83 mV at 0.1 V
s$^{-1}$ and increased to 93 mV with increase in scan speed (Table 2.10). The cathodic to anodic peak separation ($\Delta E_p$) is 175 mV at 0.1 V s$^{-1}$ which is less by 142 mV as compared to that found at pH 1.0 and is increased to 365 mV as the speed increased to 0.9 V s$^{-1}$. In all repetitive cycles, the cathodic and the anodic responses are reappeared as in the first cycle.

The cathodic peak current vs the square root of scan speed, [Plot 2.11(a, b)] is found linear and passing through origin. Similarly, the height of anodic peak increased linearly with increase in square root of scan speed and behave as diffusion controlled process.

**Table 2.10.** Cyclic voltammetric data of Eu(III)/Eu(II) couple in 0.2N CH$_3$COONa-HCl medium at pH 4.5.

<table>
<thead>
<tr>
<th>Scan speed V s$^{-1}$</th>
<th>$-E_{pc}$ V</th>
<th>$-E_{pa}$ V</th>
<th>$\Delta E_p$ mV</th>
<th>$i_{pc}$ $\mu$A</th>
<th>$i_{pa}$ $\mu$A</th>
<th>$i_{pa}/i_{pc}$</th>
<th>$E_{pa}-E_{pc}$ mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.787</td>
<td>0.612</td>
<td>175</td>
<td>3.45</td>
<td>3.26</td>
<td>0.94</td>
<td>85</td>
</tr>
<tr>
<td>0.2</td>
<td>0.801</td>
<td>0.562</td>
<td>239</td>
<td>4.54</td>
<td>3.77</td>
<td>0.83</td>
<td>92</td>
</tr>
<tr>
<td>0.5</td>
<td>0.817</td>
<td>0.520</td>
<td>297</td>
<td>7.17</td>
<td>5.19</td>
<td>0.72</td>
<td>93</td>
</tr>
<tr>
<td>0.7</td>
<td>0.820</td>
<td>0.518</td>
<td>302</td>
<td>8.36</td>
<td>5.65</td>
<td>0.68</td>
<td>90</td>
</tr>
<tr>
<td>0.9</td>
<td>0.829</td>
<td>0.468</td>
<td>361</td>
<td>9.57</td>
<td>5.91</td>
<td>0.62</td>
<td>87</td>
</tr>
</tbody>
</table>

**High scan rate.** The representative cyclic voltammograms of Eu(III) at high scan speeds (1 – 100 V s$^{-1}$) are shown in Figure 2.12 At 15 V s$^{-1}$, the Eu(III) solution exhibited a sharp cathodic peak at −0.90 V in forward scan and the corresponding anodic response at −0.352 V.

**Plot 2.12.** Plot of $i_p$ vs (a) square root of scan rate.

**Figure 2.11.** Cyclic voltammetric responses of 1 mM Eu(III)chloride solution in 0.2 N CH$_3$COONa-HCl medium at pH 4.5 at (a) 0.1; (b) 0.2; (c) 0.5; (d) 0.7 (e) 0.9 V s$^{-1}$. Temperature of the solution is 25 °C.

**Figure 2.12.** Cyclic voltammetric responses of 1 mM Eu(III) in 0.2 N CH$_3$COONa-HCl medium at pH 4.5 at scan rate (a) 15; (b) 25; (c) 50; (d) 75; (e) 100 V s$^{-1}$. Temperature of the solution is 25 °C.
in the reverse scan, [Figure 2.12(a)]. The $E_{p2}-E_p$ value for the cathodic response was 82 mV. The peak-peak separation is 627 mV, while the peak current ratio is 0.5, indicate the total irreversible nature of the electrode processes. The cyclic voltammograms recorded at other scan speeds [Figure 2.9(b-d)], indicated a cathodic shift in cathodic response and an anodic shift in the anodic response with respect to increase in scan speed. The plots of $i_{pc}$ and $i_{pa}$ vs square root of scan speed is observed linear and passing through the origin, [Plot.2.12(a, b)]. This ascertained the totally diffusion controlled nature of both the electrode process.

Table 2.11. Cyclic voltammetric data of Eu(III)/Eu(II) couple in 0.2 N CH$_3$COONa-HCl medium at pH-4.5 at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s$^{-1}$</th>
<th>$-E_{pc}$ V</th>
<th>$-E_{pa}$ V</th>
<th>$\Delta E_p$ mV</th>
<th>$i_{pc}$ $\mu$A</th>
<th>$i_{pa}$ $\mu$A</th>
<th>$i_{pa}/i_{pc}$</th>
<th>$E_{p2}-E_p$ mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.900</td>
<td>0.351</td>
<td>549</td>
<td>33.98</td>
<td>7.58</td>
<td>0.22</td>
<td>82</td>
</tr>
<tr>
<td>25</td>
<td>0.919</td>
<td>0.325</td>
<td>594</td>
<td>43.56</td>
<td>9.56</td>
<td>0.22</td>
<td>83</td>
</tr>
<tr>
<td>50</td>
<td>0.950</td>
<td>0.289</td>
<td>661</td>
<td>62.08</td>
<td>15.31</td>
<td>0.25</td>
<td>92</td>
</tr>
<tr>
<td>75</td>
<td>0.966</td>
<td>0.265</td>
<td>701</td>
<td>74.69</td>
<td>19.49</td>
<td>0.26</td>
<td>94</td>
</tr>
<tr>
<td>100</td>
<td>0.980</td>
<td>0.244</td>
<td>736</td>
<td>81.62</td>
<td>24.32</td>
<td>0.30</td>
<td>99</td>
</tr>
</tbody>
</table>

The data in Table 2.11 indicated that the position of the cathodic and anodic peaks shifted considerably and peak separation ($\Delta E_p$) is observed increasing with the increase in scan speed. Similarly, the $E_{p2}-E_p$ value for the cathodic response is 82 at 15 V s$^{-1}$ and it has increased to 99 mV at 100 V s$^{-1}$. The ratio of $i_{pa}/i_{pc}$ is found to vary between 0.22-0.30.

2.3.2. Cyclic voltammetric behaviour of Eu(III)/Eu(II) couple in aqueous unbuffered media.

Cyclic voltammograms of Eu(III) are recorded in 0.1 M solution of NaCl, KCl, LiCl, NaClO$_4$ and Na$_2$SO$_4$ respectively at their own pH (3.10-3.26) in three different scan ranges, slow (0.01–0.1 V s$^{-1}$), moderate (0.1–1.0V s$^{-1}$) and high (1-100V s$^{-1}$).

Slow scan rate. Figure 2.13 shows representative cyclic voltammograms of Eu(III) recorded at 0.03 V s$^{-1}$ in all the
above mentioned supporting electrolytes. The Eu(III) exhibits one cathodic and one anodic peak. The peak current is proportional to square root of scan rate. The values of $E_{p2}-E_p$, $\Delta E_p$ and $i_{pc}/i_{pa}$ are found to be similar to those in buffer medium at pH 2.5. Table 2.12 presents the potential data obtained at 0.03 V s$^{-1}$. The data indicates that the cathodic peaks appear in the potential range $-0.59$ to $-0.69$ V and the anodic peak appears in the range of $-0.50$ to $-0.60$ V. However, the $E_{1/2}$ values show a cathodic shift with the change in supporting electrolyte in the order of $\text{NaClO}_4 < \text{NaCl} \approx \text{KCl} < \text{LiCl} < \text{Na}_2\text{SO}_4$. The potential shift in the first four electrolytes varies from 10-30 mV, while in the case of $\text{Na}_2\text{SO}_4$ it is 86 mV. The pronounced shift in $\text{Na}_2\text{SO}_4$ medium is possibly due to complexing nature of $\text{SO}_4^{2-}$ ions.

**Table 2.12.** Cyclic voltammetric data of Eu(III)/Eu(II) couple in aqueous unbuffered medium at 0.03V s$^{-1}$, 25°C.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$E_{pc}$ V</th>
<th>$E_{pa}$ V</th>
<th>$\Delta E$ mV</th>
<th>$E_{1/2}$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NaClO}_4$</td>
<td>−0.598</td>
<td>−0.506</td>
<td>92</td>
<td>−0.552</td>
</tr>
<tr>
<td>$\text{NaCl}$</td>
<td>−0.614</td>
<td>−0.524</td>
<td>90</td>
<td>−0.564</td>
</tr>
<tr>
<td>$\text{KCl}$</td>
<td>−0.613</td>
<td>−0.523</td>
<td>90</td>
<td>−0.568</td>
</tr>
<tr>
<td>$\text{LiCl}$</td>
<td>−0.625</td>
<td>−0.534</td>
<td>91</td>
<td>−0.579</td>
</tr>
<tr>
<td>$\text{Na}_2\text{SO}_4$</td>
<td>−0.684</td>
<td>−0.593</td>
<td>91</td>
<td>−0.638</td>
</tr>
</tbody>
</table>

*Moderate scan rate.* Cyclic voltammograms of Eu(III) at moderate scan rate in different supporting electrolytes shows a single cathodic peak in the forward scan and two anodic peaks in the reverse scan as shown in Figure 2.14 at 0.7 V s$^{-1}$. As found in case of buffered medium at pH 2.5, the heights of these peaks, increase with the increase in square root of scan speed. The peak potentials at 0.7 V s$^{-1}$ are in the range from $-0.64$ V to $-0.72$ V for cathodic, $-0.50$ V to $-0.59$ V for $E_{a1}$ and $-0.10$ V to $-0.27$ V for $E_{a2}$. The potential shifts (Table 2.13) observed with the change in supporting electrolyte are coinciding with those found in slow scan range (Table 2.12).
Table 2.13. Cyclic voltammetric data of Eu(III)/Eu(II) couple in aqueous unbuffered medium at 0.7 V s⁻¹, at 25°C.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Epc</th>
<th>Epa1</th>
<th>Epa2</th>
<th>ΔE₁</th>
<th>ΔE₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO₄</td>
<td>−0.640</td>
<td>−0.504</td>
<td>−0.108</td>
<td>136</td>
<td>532</td>
</tr>
<tr>
<td>NaCl</td>
<td>−0.657</td>
<td>−0.523</td>
<td>−0.184</td>
<td>134</td>
<td>473</td>
</tr>
<tr>
<td>KCl</td>
<td>−0.659</td>
<td>−0.520</td>
<td>−0.162</td>
<td>139</td>
<td>497</td>
</tr>
<tr>
<td>LiCl</td>
<td>−0.677</td>
<td>−0.526</td>
<td>−0.150</td>
<td>151</td>
<td>527</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>−0.718</td>
<td>−0.591</td>
<td>−0.276</td>
<td>127</td>
<td>442</td>
</tr>
</tbody>
</table>

High scan rate. Cyclic voltammetric responses of Eu(III) recorded at 25 V s⁻¹ in NaCl, KCl, LiCl, NaClO₄ and Na₂SO₄ respectively are shown in Figure 2.15. In NaClO₄, Eu(III) shows a single cathodic peak at −0.810 V identical to that in Figures 2.13 and 2.14 and a single anodic peak E₀₂ at −0.028 V. The anodic peak has shifted to anodic potentials with further increase in scan rate. Moreover, the peak positions are found to shift with the change in supporting electrolyte in the order of NaClO₄ < NaCl ≈ KCl < LiCl < Na₂SO₄ in identical manner to that observed at slow scan rates.

2.3.3. Cyclic voltammetric behavior of Eu(III)/Eu(II) couple in aquo-organic media.

50:50-MeOH-water. Slow scan rate. The cyclic voltammetric responses of the Eu(III) at different scan rates (0.01, 0.02, 0.05 and 0.1 V s⁻¹) are shown in Figure 2.16(a–d), The response at 0.01 V s⁻¹ showed a single cathodic peak at −0.606 V in the forward scan and a single...
anodic peak at $-0.541$ V in the reverse scan. The peak separation is 65 mV and the anodic to cathodic peak current ratio is 0.89, which is less than one, indicating that the electrode process is nearly reversible. However, the $E_{p/2}-E_p$ value for the cathodic response is nearly constant at 63 mV, and the ratio, $i_{pa}/i_{pc}$ is found decreasing with the increase in scan rate. The plots of $i_{pc}$ and $i_{pa}$ vs square root of scan speed ($\sqrt{v}$) is linear and passing through the origin. This ascertained the totally diffusion controlled nature of both the electrode process. The $E_{1/2}$ value for the Eu(III)/Eu(II) couple as estimated from $(E_{pc}+E_{pa})/2$ has shifted from $-0.573$ at 0.01 V s$^{-1}$ to $-0.542$ V at 0.1 V s$^{-1}$.

**Table 2.14.** Cyclic voltammetric data of Eu(III)/Eu(II) couple in 50:50 MeOH-water medium at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s$^{-1}$</th>
<th>$-E_{pc}$ V</th>
<th>$-E_{pa}$ V</th>
<th>$\Delta E_p$ mV</th>
<th>$i_{pa}/i_{pc}$</th>
<th>$-E_{1/2}$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.606</td>
<td>0.541</td>
<td>65</td>
<td>0.73</td>
<td>0.573</td>
</tr>
<tr>
<td>0.02</td>
<td>0.607</td>
<td>0.515</td>
<td>92</td>
<td>0.59</td>
<td>0.560</td>
</tr>
<tr>
<td>0.05</td>
<td>0.617</td>
<td>0.482</td>
<td>135</td>
<td>0.48</td>
<td>0.549</td>
</tr>
<tr>
<td>0.1</td>
<td>0.631</td>
<td>0.454</td>
<td>177</td>
<td>0.53</td>
<td>0.542</td>
</tr>
</tbody>
</table>

*Moderate scan rate.* The cyclic voltammograms of Eu(III) recorded at moderate scan rates are shown in Figure 2.17(a-d). The solution exhibited a single cathodic peak ($-0.636$ V at 0.2 V s$^{-1}$) in the forward scan. On the other hand, a new broad and diffusive anodic peak is observed at $-0.221$ V with the disappearance of the anodic peak-1. This indicates that both the peaks observed at slow and moderate scan rates are two different kinds of species of Eu(II) formed at the electrode surface during this electrochemical process. The new anodic response at $-0.221$ V is observed to shift anodically with the increase in scan speed. The peak separation ($\Delta E_p$) is observed to be 415 mV at 0.2 V s$^{-1}$ and increased to 508 mV at 0.9 V s$^{-1}$ (Table 2.15) indicating that the Eu(III)/Eu(II) couple is totally
irreversible in the investigated scan range. The plots of $i_p$ vs square root of scan speed ($v^{1/2}$) is linear and passing through the origin. This indicated the totally diffusion controlled nature of the electrode process. However, the cathodic and the anodic peaks are repeatedly observed in their all subsequent cycles indicate the irreversible nature of Eu(III) due to the complex behavior of the europium ions.

Table 2.15. Cyclic voltammetric data of Eu(III)/Eu(II) couple in 50:50 MeOH-water medium at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s$^{-1}$</th>
<th>$-E_{pc}$ V</th>
<th>$-E_{pa}$ V</th>
<th>$\Delta E_p$ mV</th>
<th>$i_{pc}$ $\mu$A</th>
<th>$i_{pa}$ $\mu$A</th>
<th>$i_{pa}/i_{pc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.636</td>
<td>0.221</td>
<td>415</td>
<td>4.224</td>
<td>0.100</td>
<td>0.02</td>
</tr>
<tr>
<td>0.5</td>
<td>0.653</td>
<td>0.173</td>
<td>480</td>
<td>6.495</td>
<td>0.147</td>
<td>0.07</td>
</tr>
<tr>
<td>0.7</td>
<td>0.659</td>
<td>0.162</td>
<td>497</td>
<td>7.343</td>
<td>0.846</td>
<td>0.12</td>
</tr>
<tr>
<td>0.9</td>
<td>0.663</td>
<td>0.155</td>
<td>508</td>
<td>8.530</td>
<td>1.212</td>
<td>0.14</td>
</tr>
</tbody>
</table>

*High scan rate.* The cyclic voltammograms of EuCl$_3$ are recorded at high scan rates (10 to 25 V s$^{-1}$) in 50:50 MeOH-water [Figure 2.18 (a-d)]. At 10 V s$^{-1}$, the solution exhibited a well defined single cathodic peak at 0.720 V in forward scan and a single anodic peak at 0.065 V in the reverse scan. The cathodic response is sharp and shifted cathodically with increase in scan rate. However, the fairly sharp anodic peak shifted to anodic potentials as the scan rate increased. As a result, the cathodic to anodic peak separation ($\Delta E_p$) is found increased from 655mV to 723 mV (Table 2.16) the increasing irreversible character of the Eu(III)/Eu(II) couple. The cathodic and the anodic responses are recorded repeatedly and observed reproducibility.

This indicates the absence of adsorption and other complex electrode phenomenon associated to oxidation-reduction steps. The $i_{pa}/i_{pc}$ is also less than unity at all scan rates indicating the irreversible nature of Eu(III)/Eu(II) couple in the present medium at these scan rates.

Figure 2.18. Cyclic voltammetric responses of 1 mM Eu(III) in 0.1 M NaClO$_4$ in 50:50 MeOH-water medium at scan rate (a) 10; (b) 15; (c) 20; (d) 25; V s$^{-1}$. Temperature of the solution is 25°C.
**Table 2.16.** Cyclic voltammetric data of Eu(III)/Eu(II) couple in 70:30 MeOH-water medium at 25°C.

<table>
<thead>
<tr>
<th>Scan rate $V_s^{-1}$</th>
<th>$-E_{pc}$ V</th>
<th>$-E_{pa}$ V</th>
<th>$\Delta E_p$ mV</th>
<th>$i_{pc}$ $\mu A$</th>
<th>$i_{pa}$ $\mu A$</th>
<th>$i_{pa}/i_{pc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.720</td>
<td>0.065</td>
<td>655</td>
<td>25.82</td>
<td>9.16</td>
<td>0.35</td>
</tr>
<tr>
<td>15</td>
<td>0.734</td>
<td>0.051</td>
<td>683</td>
<td>30.31</td>
<td>11.20</td>
<td>0.37</td>
</tr>
<tr>
<td>20</td>
<td>0.744</td>
<td>0.033</td>
<td>711</td>
<td>36.21</td>
<td>14.00</td>
<td>0.38</td>
</tr>
<tr>
<td>25</td>
<td>0.749</td>
<td>0.026</td>
<td>723</td>
<td>37.36</td>
<td>14.14</td>
<td>0.38</td>
</tr>
</tbody>
</table>

The plots of $i_{pc}$ and $i_{pa}$ vs square root of scan speed ($v^{1/2}$) are linear and passing through the origin. This ascertained the totally diffusion controlled nature of both the electrode process.

70:30 MeOH-water medium. Slow scan rate.

The cyclic voltammetric response of Eu(III) solution in 70:30 MeOH-water at scan rate of 0.01 V s$^{-1}$, exhibited a single-sharp cathodic peak at $-0.650$ V in the forward scan and a single and fairly well defined anodic peak at $-0.540$ V in the reverse scan as shown in Figure 2.19(a). The peak separation is 110 mV and the anodic to cathodic peak current ratio is 0.96, indicating that the electrode process is quasi reversible. As the scan speed increases to 0.1 V s$^{-1}$, the cathodic peak is sharp and increased in height with the increase in scan rate. On the other hand, the anodic peak increased with the increase in scan rate and turned to be broad due to

**Figure 2.19.** Cyclic voltammetric responses of 1 mM Eu(III) in 0.1M NaClO$_4$ in 70:30 MeOH-water at scan rate (a) 0.01; (b) 0.02; (c) 0.05; (d) 0.1 V s$^{-1}$. Temperature of the solution is 25°C

**Table 2.17.** Cyclic voltammetric data of Eu (III)/Eu (II) couple in 70:30 MeOH-water at 25 °C.

<table>
<thead>
<tr>
<th>Scan rate $V_s^{-1}$</th>
<th>$-E_{pc}$ V</th>
<th>$-E_{pa}$ V</th>
<th>$\Delta E_p$ mV</th>
<th>$i_{pa}/i_{pc}$</th>
<th>$-E_{1/2}$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.650</td>
<td>0.540</td>
<td>110</td>
<td>0.96</td>
<td>0.595</td>
</tr>
<tr>
<td>0.02</td>
<td>0.652</td>
<td>0.525</td>
<td>127</td>
<td>0.89</td>
<td>0.588</td>
</tr>
<tr>
<td>0.05</td>
<td>0.664</td>
<td>0.440</td>
<td>224</td>
<td>0.65</td>
<td>0.552</td>
</tr>
<tr>
<td>0.08</td>
<td>0.673</td>
<td>0.437</td>
<td>236</td>
<td>0.58</td>
<td>0.555</td>
</tr>
</tbody>
</table>
the appearance of a new peak at −0.35 V. The cyclic voltammetric data are given in Table 2.17.

As seen in the table, a cathodic shift in the cathodic peak potential and anodic shift in the anodic peak potential is noticed with the increase in scan rate. Subsequently, the value of peak separation ($\Delta E_p$) increased with increase in sweep rates. On the contrary, the $E_{p/2}$ value for cathodic response was 52 mV and remained constant at other scan rates. The plots of $i_p$ vs square root of scan speed ($\sqrt{v}$) are linear and passing through the origin, this indicating the process is totally diffusion controlled.

The $E_{1/2}$ value for the Eu(III)/Eu(II) couple as estimated from $(E_{pc} + E_{pa})/2$ is varied from −0.595 to −0.555 V with increase in scan rate.

*Moderate scan rate.* The cyclic voltammograms of EuCl$_3$ solution recorded in 70:30 MeOH-water at moderate scan rates are shown in Figure 2.20(a–d). The metal Eu(III) exhibited a single cathodic peak in forward scan and a single anodic peak in the reverse scan. The cathodic and anodic responses are fairly sharp and shifted respectively with increase in scan rate. The cathodic to anodic peak separation ($\Delta E_p$) is 290 mV at 0.1 V s$^{-1}$ and it increased to 437 mV as the speed increases to 0.9 V s$^{-1}$ (Table 2.18). The cathodic and the anodic responses are observed repeatedly when the potential scan was continued indicating the absence of adsorption and other phenomenon associated with the electrode process. The plots of $i_{pc}$ and $i_{pa}$ vs square root of scan speed ($\sqrt{v}$) is linear and passed through the origin. This ascertained the totally diffusion controlled nature of both the electrode process. The $i_{pa}/i_{pc}$ is also less than unity at all scan rates indicating the irreversible nature of Eu(III)/Eu(II) couple in the present medium.
Table 2.18. Cyclic voltammetric data of Eu(III)/Eu(II) couple in 70:30 MeOH-water medium at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s⁻¹</th>
<th>-Epc V</th>
<th>-Epa V</th>
<th>ΔEp mV</th>
<th>ipc μA</th>
<th>ipa μA</th>
<th>ipa/ipc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.677</td>
<td>0.387</td>
<td>290</td>
<td>4.731</td>
<td>0.518</td>
<td>0.11</td>
</tr>
<tr>
<td>0.3</td>
<td>0.700</td>
<td>0.318</td>
<td>382</td>
<td>7.828</td>
<td>0.890</td>
<td>0.13</td>
</tr>
<tr>
<td>0.7</td>
<td>0.718</td>
<td>0.294</td>
<td>424</td>
<td>11.96</td>
<td>3.617</td>
<td>0.30</td>
</tr>
<tr>
<td>0.9</td>
<td>0.723</td>
<td>0.286</td>
<td>437</td>
<td>13.52</td>
<td>5.366</td>
<td>0.40</td>
</tr>
</tbody>
</table>

High scan rate. The cyclic voltammograms of EuCl₃ recorded at high scan (10 to 25.0 V s⁻¹) rates in 70:30 MeOH-water are shown in Figure 2.21(a-d). The solution exhibited a well defined single cathodic peak at −0.800 V in forward scan and a single anodic peak −0.222 V in the reverse scan at 10 V s⁻¹. The cathodic response is sharp and shifted cathodically with the increase in scan rate. The anodic peak is also fairly sharp and shifted to anodic potentials as the scan rate increases. As a result, the cathodic to anodic peak separation (ΔEp) is increased from 578 mV to 663 mV (Table 2.19). The i_{pa}/i_{pc} is also less than unity at all scan rates indicating the irreversible nature of Eu(III)/Eu(II) couple in the present medium at these scan rates. The plots of i_{pc} and i_{pa} vs square root of scan speed (v^{1/2}) is linear and passed through the origin, this ascertained the totally diffusion controlled nature of both the electrode process.

Table 2.19. Cyclic voltammetric data of Eu(III)/Eu(II) couple in 70-30 MeOH-water medium at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s⁻¹</th>
<th>-Epc V</th>
<th>-Epa V</th>
<th>ΔEp mV</th>
<th>ipc μA</th>
<th>ipa μA</th>
<th>i_{pa}/i_{pc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.800</td>
<td>0.222</td>
<td>578</td>
<td>39.78</td>
<td>22.79</td>
<td>0.57</td>
</tr>
<tr>
<td>15</td>
<td>0.815</td>
<td>0.201</td>
<td>614</td>
<td>45.54</td>
<td>26.47</td>
<td>0.58</td>
</tr>
<tr>
<td>20</td>
<td>0.831</td>
<td>0.190</td>
<td>641</td>
<td>50.69</td>
<td>29.83</td>
<td>0.58</td>
</tr>
<tr>
<td>25</td>
<td>0.848</td>
<td>0.185</td>
<td>663</td>
<td>56.51</td>
<td>33.43</td>
<td>0.59</td>
</tr>
</tbody>
</table>
50:50 DMF-water medium.

Slow scan rate. The E-i responses of Eu(III) solution in 50:50 DMF water at 0.01 V s\(^{-1}\) [Figure 2.22(a)]. Eu(III) exhibited a single cathodic peak at \(-0.653\) V in the forward scan and the corresponding anodic peak at \(-0.575\) V in the reverse scan. The \(E_{p/2}-E_p\) value obtained for cathodic peak is 57 mV, which confirmed the reduction process as one electron step. The peak separation is 78 mV while the anodic to cathodic peak current ratio as 0.96, indicating that the electrode process is quasi reversible. Similar response is noticed at other scan rates (0.03, 0.05 and 0.1 V s\(^{-1}\)) [Figure 2.22(b-d)]. The cyclic voltammetric data are given in Table 2.20. A negligible shift in cathodic and anodic peak positions, a slight increase in \(\Delta E_p\) value and no change in \(E_{p/2}-E_p\) value are noticed with increase in the scan rates. The plots of \(i_{pc}\) and \(i_{pa}\) vs square root of scan speed (\(v^{1/2}\)) are linear and passed through the origin. It indicates that the diffusion controlled. However, the peak current ratio (\(i_{pa}/i_{pc}\)) showed a decreasing of the trend. The measured \(E_{1/2}\) value (vs Ag/AgCl) for Eu(III)/Eu(II) couple estimated from \((E_{pc}+E_{pa})/2\) is 0.614 V.

**Table 2.20.** Cyclic voltammetric data of Eu (III)/Eu (II) couple in 50:50 DMF-water at 25 °C.

<table>
<thead>
<tr>
<th>Scan rate V s(^{-1})</th>
<th>(-E_{pc}) V</th>
<th>(-E_{pa}) V</th>
<th>(\Delta E_p) mV</th>
<th>(i_{pa}/i_{pc})</th>
<th>(-E_{1/2}) V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.653</td>
<td>0.565</td>
<td>78</td>
<td>0.96</td>
<td>0.614</td>
</tr>
<tr>
<td>0.03</td>
<td>0.654</td>
<td>0.574</td>
<td>80</td>
<td>0.97</td>
<td>0.614</td>
</tr>
<tr>
<td>0.05</td>
<td>0.659</td>
<td>0.571</td>
<td>88</td>
<td>0.98</td>
<td>0.615</td>
</tr>
<tr>
<td>0.10</td>
<td>0.661</td>
<td>0.568</td>
<td>93</td>
<td>0.95</td>
<td>0.614</td>
</tr>
</tbody>
</table>
**Moderate scan rate.** The cyclic voltammograms of EuCl₃ are recorded at moderate scan (0.1 to 1.0 V s⁻¹) rates in 50:50 DMF-water are shown in Figure 2.23(a-d). The solution exhibited a well defined single cathodic peak at −0.669 V in forward scan and a single anodic peak at −0.566 V in the reverse scan at 0.2 V s⁻¹. The cathodic response is sharp and shifted cathodically with the increase in scan speed. The anodic peak is fairly sharp and shifted to anodic potentials with increases in scan rate. As a result, the cathodic to anodic peak separation (ΔE_p) is increased from 103 mV at 0.2 V s⁻¹ to 144 mV at 1.0 V s⁻¹ (Table 2.21). The cathodic and the anodic responses are appeared reproducible indicating the absence of adsorption and other phenomenon associated with the electrode process. The i_p/a/i_p is also less than unity at all scan rates indicating nearly reversible nature of Eu(III)/Eu(II) couple in the studied medium. The plots of i_p and i_a vs square root of scan speed (v^{1/2}) is found linear and passed through the origin this ascertained the totally diffusion controlled nature of both the electrode process.

**Table 2.21.** Cyclic voltammetric data of Eu(III)/Eu(II) couple in 50:50 DMF-water medium at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s⁻¹</th>
<th>-E_p V</th>
<th>-E_a V</th>
<th>ΔE_p mV</th>
<th>i_p μA</th>
<th>i_a μA</th>
<th>i_a/i_p</th>
<th>-E_1/2 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.669</td>
<td>0.566</td>
<td>103</td>
<td>3.320</td>
<td>3.116</td>
<td>0.93</td>
<td>0.617</td>
</tr>
<tr>
<td>0.3</td>
<td>0.674</td>
<td>0.563</td>
<td>111</td>
<td>3.910</td>
<td>3.672</td>
<td>0.94</td>
<td>0.618</td>
</tr>
<tr>
<td>0.7</td>
<td>0.686</td>
<td>0.554</td>
<td>132</td>
<td>5.908</td>
<td>5.448</td>
<td>0.92</td>
<td>0.620</td>
</tr>
<tr>
<td>1.0</td>
<td>0.694</td>
<td>0.550</td>
<td>144</td>
<td>6.648</td>
<td>6.425</td>
<td>0.96</td>
<td>0.622</td>
</tr>
</tbody>
</table>

**High scan rate.** The cyclic voltammograms of EuCl₃ are recorded at high scan rates (10 to 25 V s⁻¹) in 50:50 DMF-water medium. At 10 V s⁻¹, the solution exhibited a well defined single cathodic peak at −0.789 V in forward scan and a single anodic peak at −0.475 V in the reverse scan. The cathodic response is fairly sharp and shifted cathodically with the increase in
scan speed. However, the fairly sharp anodic peak shifted to anodic potentials as the scan rate increased.

Table 2.22. Cyclic voltammetric data of Eu(III)/Eu(II) couple in 50:50 DMF-water medium at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s(^{-1})</th>
<th>(-E_{pc}) V</th>
<th>(-E_{pa}) V</th>
<th>(\Delta E_{p}) mV</th>
<th>(i_{pc}) (\mu)A</th>
<th>(i_{pa}) (\mu)A</th>
<th>(i_{pa}/i_{pc})</th>
<th>(-E_{1/2}) V</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.789</td>
<td>0.475</td>
<td>314</td>
<td>26.40</td>
<td>14.22</td>
<td>0.54</td>
<td>0.632</td>
</tr>
<tr>
<td>15</td>
<td>0.819</td>
<td>0.457</td>
<td>362</td>
<td>31.13</td>
<td>16.02</td>
<td>0.51</td>
<td>0.638</td>
</tr>
<tr>
<td>20</td>
<td>0.844</td>
<td>0.439</td>
<td>405</td>
<td>35.34</td>
<td>19.53</td>
<td>0.55</td>
<td>0.641</td>
</tr>
<tr>
<td>25</td>
<td>0.866</td>
<td>0.419</td>
<td>447</td>
<td>38.50</td>
<td>20.90</td>
<td>0.54</td>
<td>0.642</td>
</tr>
</tbody>
</table>

As a result, the cathodic to anodic peak separation (\(\Delta E_{p}\)) is increased from 314 mV to 447 mV (Table 2.22). The cathodic and the anodic responses are appeared repeatedly when the potential scan was continued for 5-6 times repetitively. This indicates the absence of adsorption and other complex electrode phenomenon associated to oxidation-reduction steps. The plots of \(i_{p}\) vs square root of scan rates (\(v^{1/2}\)) is linear and passed through the origin. This indicated that the Eu (III) reduction and the subsequent oxidation process are diffusion controlled. The \(i_{pa}/i_{pc}\) is also less than unity at all scan rates indicating the borderline case of irreversible to quasi reversible nature of Eu(III)/Eu(II) couple.

70:30 DMF-water medium. Slow scan rate. The cyclic voltammograms of Eu(III) solution in 70:30 DMF-water at 0.01 V s\(^{-1}\), exhibited a single well defined cathodic peak at \(-0.672\) V in the forward scan and the corresponding well defined anodic peak at \(-0.600\) V in the reverse scan [Figure 2.24(a)]. The peak separation is only 72 mV while the anodic to cathodic peak current ratio was 0.91, indicating that the electrode process is quasi reversible. Similar response could be seen at other scan rates (0.02, 0.03 and 0.05 V s\(^{-1}\)) [Figure 2.24(b-d)]. The cyclic voltammograms of 1 mM Eu(III) in 0.1M TEABF\(_4\) in70:30 DMF-water at scan rates (a) 0.01; (b) 0.02; (c) 0.03; (d) 0.05 V s\(^{-1}\). Temperature of the solution is 25 °C.
voltammetric data are given in Table 2.23. A negligible change in cathodic and anodic peak potentials and a slight increase in peak to peak separation (ΔE_p) are noticed with increase in sweep rates. Also, the E_p/2–E_p value for cathodic response is almost steady at 52 mV. The plots of i_(pc) and i_(pa) vs square root of scan rates (v^1/2) is found linear and passed through the origin. This indicated that the Eu (III) reduction and the subsequent oxidation process are diffusion controlled. The E_(1/2) value for the Eu(III)/Eu(II) couple as estimated from (E_(pc)+E_(pa))/2 is almost constant at 0.634 V at all scan rates.

Table 2.23. Cyclic voltammetric data of Eu (III)/Eu (II) couple in 70:30 DMF-water at 25 °C.

<table>
<thead>
<tr>
<th>Scan rate (V s⁻¹)</th>
<th>E_(pc) (V)</th>
<th>E_(pa) (V)</th>
<th>ΔE_p (mV)</th>
<th>i_p/ i_(pc)</th>
<th>E_(1/2) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.672</td>
<td>0.600</td>
<td>72</td>
<td>0.91</td>
<td>0.636</td>
</tr>
<tr>
<td>0.02</td>
<td>0.674</td>
<td>0.593</td>
<td>81</td>
<td>0.96</td>
<td>0.633</td>
</tr>
<tr>
<td>0.03</td>
<td>0.676</td>
<td>0.592</td>
<td>84</td>
<td>0.90</td>
<td>0.634</td>
</tr>
<tr>
<td>0.05</td>
<td>0.679</td>
<td>0.590</td>
<td>89</td>
<td>0.92</td>
<td>0.634</td>
</tr>
</tbody>
</table>

*Moderate scan rate.* The cyclic voltammograms of EuCl₃ solution recorded in 70:30 DMF-water at moderate scan rates are shown in Figure 2.25. The metal, Eu(III) exhibited a single cathodic peak at −0.693 V in the forward scan and a single anodic peak at −0.584 V in the reverse scan at 0.2 V s⁻¹. Both cathodic and anodic peaks shown shift with increase in scan rate cathodically and anodically respectively. The peak-peak separation (ΔE_p) is found 109 mV at 0.2 V s⁻¹ and it increased to 149 mV as the scan speed increased to 0.9 V s⁻¹ (Table 2.24). The cathodic and the anodic responses were appeared repeatedly when the potential scan was continued to 5-6 times indicating the absence of adsorption and other complex electrode phenomenon associated with
the Eu(III)/Eu(II) couple. The plots of $i_{pc}$ and $i_{pa}$ vs square root of scan rates ($\sqrt{v}$) is linear and passed through the origin. This indicated that the Eu (III) reduction and the subsequent oxidation process are diffusion controlled. The $i_{pa}/i_{pc}$ is also less than unity at all scan rates indicating the nearly reversible nature of Eu(III)/Eu(II) couple in the present medium.

**Table 2.24.** Cyclic voltammetric data of Eu(III)/Eu(II) couple in 70:30 DMF-water medium at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s$^{-1}$</th>
<th>$-E_{pc}$ V</th>
<th>$-E_{pa}$ V</th>
<th>$\Delta E_p$ mV</th>
<th>$i_{pc}$ $\mu$A</th>
<th>$i_{pa}$ $\mu$A</th>
<th>$i_{pa}/i_{pc}$</th>
<th>$-E_{1/2}$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.693</td>
<td>0.584</td>
<td>109</td>
<td>4.244</td>
<td>3.503</td>
<td>0.83</td>
<td>0.617</td>
</tr>
<tr>
<td>0.5</td>
<td>0.709</td>
<td>0.575</td>
<td>134</td>
<td>6.649</td>
<td>5.120</td>
<td>0.77</td>
<td>0.618</td>
</tr>
<tr>
<td>0.7</td>
<td>0.715</td>
<td>0.573</td>
<td>142</td>
<td>7.671</td>
<td>5.966</td>
<td>0.77</td>
<td>0.620</td>
</tr>
<tr>
<td>0.9</td>
<td>0.722</td>
<td>0.571</td>
<td>149</td>
<td>8.594</td>
<td>6.716</td>
<td>0.78</td>
<td>0.622</td>
</tr>
</tbody>
</table>

*High scan rate.* The cyclic voltammograms of EuCl$_3$ are recorded at high scan rates (10 to 25.0 V s$^{-1}$) in 70:30 DMF-water. At 10 V s$^{-1}$, the solution exhibited a well defined single cathodic peak at $-0.830$ V in forward scan and a single anodic peak $-0.489$ V in the reverse scan. The cathodic response is fairly sharp and shifted cathodically with the increase in scan speed. However the fairly sharp anodic peak shifted to anodic potentials as the scan rate increases to 25 V s$^{-1}$ (Table 2.25). As a result, the cathodic to anodic peak separation ($\Delta E_p$) is increased from 341 mV to 0.484 mV. In all repetitive cycles, the cathodic and the anodic responses are appeared repetitive when the potential scan is continued indicate the absence of adsorption and other complicated electrode phenomenon associated with the Eu(III)/Eu(II) couple.

**Table 2.25.** Cyclic voltammetric data of Eu(III)/Eu(II) couple in 70:30 DMF-water medium at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s$^{-1}$</th>
<th>$-E_{pc}$ V</th>
<th>$-E_{pa}$ V</th>
<th>$\Delta E_p$ mV</th>
<th>$i_{pc}$ $\mu$A</th>
<th>$i_{pa}$ $\mu$A</th>
<th>$i_{pa}/i_{pc}$</th>
<th>$-E_{1/2}$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.830</td>
<td>0.489</td>
<td>341</td>
<td>24.63</td>
<td>15.19</td>
<td>0.62</td>
<td>0.659</td>
</tr>
<tr>
<td>15</td>
<td>0.864</td>
<td>0.468</td>
<td>396</td>
<td>28.91</td>
<td>17.92</td>
<td>0.62</td>
<td>0.666</td>
</tr>
<tr>
<td>20</td>
<td>0.891</td>
<td>0.446</td>
<td>445</td>
<td>32.05</td>
<td>19.72</td>
<td>0.62</td>
<td>0.668</td>
</tr>
<tr>
<td>25</td>
<td>0.914</td>
<td>0.430</td>
<td>484</td>
<td>34.95</td>
<td>21.86</td>
<td>0.62</td>
<td>0.672</td>
</tr>
</tbody>
</table>

The plots of $i_p$ vs square root of scan rates ($\sqrt{v}$) is linear and passed through the origin. This indicated that the Eu (III) reduction and the subsequent oxidation process are diffusion controlled. The $i_{pa}/i_{pc}$ is also observed less than unity at all scan rates indicating the irreversible nature of Eu(III)/Eu(II) couple in the present medium at these scan rates. The $E_{1/2}$ value for the
Eu(III)/Eu(II) couple as estimated from \((E_{pc} + E_{pa})/2\) is found to shift from \(-0.659 \text{ V}\) to \(-0.672 \text{ V}\) with increase in scan rate.

50:50 CH\(_3\)CN-water. Slow scan rate.

The E-i responses of Eu(III) solution in 50:50 CH\(_3\)CN-water using 0.1M NaClO\(_4\) solution as supporting electrolyte and recorded at different scan speeds ranges from 0.01V s\(^{-1}\) to 0.08 V s\(^{-1}\) are shown in Figure 2.26(a). Unlike in 50:50 or 70:30 DMF-water, the metal, Eu(III) exhibited a single cathodic peak at more negative potentials \(-0.783 \text{ V}\) in the forward scan and a less intensive broad anodic peak at \(-0.664 \text{ V}\) in the reverse scan. Similar response is observed at other slow scan rates (0.02, 0.05 and 0.08 V s\(^{-1}\)) [Figure 2.26(b-d)]. The peak separation \(\Delta E_p\) is found from 119 mV to 195 mV [Table 2.26] while the anodic to cathodic peak current ratio of 0.56, which is less than one, indicating that the electrode process is irreversible. However, the ratio, \(i_{pa}/i_{pc}\), is decreasing with the increase in scan rate. The \(E_{1/2}\) value for the Eu(III)/Eu(II) couple as estimated from \((E_{pc} + E_{pa})/2\) is from \(-0.723 \text{ V}\) to \(-0.700 \text{ V}\).

**Table 2.26.** Cyclic voltammetric data of Eu(III)/Eu(II) couple in 50:50 CH\(_3\)CN-water medium at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s(^{-1})</th>
<th>(-E_{pc}) V</th>
<th>(-E_{pa}) V</th>
<th>(\Delta E_p) mV</th>
<th>(i_{pa}/i_{pc})</th>
<th>(-E_{1/2}) V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.783</td>
<td>0.664</td>
<td>119</td>
<td>0.56</td>
<td>0.723</td>
</tr>
<tr>
<td>0.02</td>
<td>0.791</td>
<td>0.659</td>
<td>132</td>
<td>0.67</td>
<td>0.725</td>
</tr>
<tr>
<td>0.05</td>
<td>0.793</td>
<td>0.623</td>
<td>170</td>
<td>0.36</td>
<td>0.708</td>
</tr>
<tr>
<td>0.08</td>
<td>0.795</td>
<td>0.600</td>
<td>195</td>
<td>0.16</td>
<td>0.700</td>
</tr>
</tbody>
</table>

Moderate scan rate. The cyclic voltammograms of EuCl\(_3\) solution recorded in 50:50 CH\(_3\)CN-water at moderate scan rates (0.2, 0.3, 0.7 and 0.9 V s\(^{-1}\)) are shown in Figure 2.27(a-d). Eu(III) exhibited a single well defined cathodic peak at \(-0.808 \text{ V}\) in the forward scan and no anodic peak in the reverse scan at 0.2 V s\(^{-1}\), indicating the irreversible one-electron reduction of
Eu(III) in 50:50 CH$_3$CN-water. The cathodic response is sharp and shifted cathodically with the increase in scan rate. However, the $E_{p/2}$–$E_{p}$ value for the cathodic response was nearly constant at 63 mV, confirming this as one electron process.

**Table 2.27.** Cyclic voltammetric data of Eu(III)/Eu(II) couple in 70:30 CH$_3$CN-water medium at 25°C.

<table>
<thead>
<tr>
<th>Scan rate V s$^{-1}$</th>
<th>$-E_{pc}$ V</th>
<th>$-E_{pc1/2}$ V</th>
<th>$i_{pc}$ $\mu$A</th>
<th>$E_{p/2}$–$E_{p}$ mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.808</td>
<td>0.745</td>
<td>5.228</td>
<td>63</td>
</tr>
<tr>
<td>0.3</td>
<td>0.820</td>
<td>0.753</td>
<td>6.127</td>
<td>67</td>
</tr>
<tr>
<td>0.7</td>
<td>0.830</td>
<td>0.763</td>
<td>7.505</td>
<td>67</td>
</tr>
<tr>
<td>0.9</td>
<td>0.841</td>
<td>0.772</td>
<td>9.346</td>
<td>69</td>
</tr>
</tbody>
</table>

*High scan rate.* The cyclic voltammetric responses of EuCl$_3$ solution recorded at high scan rate range in 50:50 CH$_3$CN-water are quite similar to those obtained in case of moderate scan rates. Hence, for avoiding the repetition, they are not further considered.

**70:30 CH$_3$CN-water.** The cyclic voltammograms of EuCl$_3$ solution recorded in 70:30 CH$_3$CN-water at slow scan rates (0.02, 0.03, 0.05 and 0.1 V s$^{-1}$) are shown in Figure 2.28(a-d). The metal Eu(III) exhibited a single well defined cathodic peak at $-0.726$ V in the forward scan and no anodic peak in the reverse scan at 0.02 V s$^{-1}$. Additionally, a pre peak due adsorption at
about −0.44 V are observed at all scan rates. Similar behavior of peaks are observed in absence of Eu(III), confirming the pre peak is due to the adsorption caused by high acetonitrile composition. The cathodic response at −0.726 V is sharp and shifted cathodically with the increase in scan rate. However, the $E_{p/2} - E_p$ value for the cathodic response is nearly constant at 63 mV, indicating involvement of single electron transfer.

The cyclic voltammetric responses of EuCl$_3$ solution recorded at moderate and high scan rate ranges in 70:30 CH$_3$CN-water are quite similar to those explained at slow scan rates and hence not considered, for the discussion.

2.3.4. Chronopotentiometry of Eu(III) medium. The chronopotentiograms of Eu(III) are recorded for both cathodic and anodic processes at pH-2.5 in NaCl-HCl medium. The cathodic segments are recorded after adjusting potential in the range from −0.2 V to −1.0 V and different cathodic current are applied in the range from 2.5 μA to 5.0 μA, [Figure 2.30(a-f)]. Chronopotentiograms of Eu(III)
in the cathodic process showed a single plateau. The transition time \( \tau \) obtained for the forward process is 4.35 seconds at 2.5 \( \mu \text{A} \) and found shifted (form 4.35 to 0.45 sec) with decrease in cathodic current (form 5.0 \( \mu \text{A} \) to2.5 \( \mu \text{A} \)). The linear behavior of plot of \( i \) vs \( 1/\tau^{1/2} \) clearly suggest the reduction of Eu(III) to Eu(II) is governed by diffusion process and not affected by other complications.

In case of reverse scan, the potentials are fixed in the range from \( -0.1 \) to \( -1.2 \) V and the anodic current is varied from 0.25 \( \mu \text{A} \) to 2.5 \( \mu \text{A} \). The Chronopotentiogram showed two plateaus (P1 and P2) at pH-2.5 one observed at 4.20 sec. and another at 1.90 sec at 0.25 \( \mu \text{A} \). This behavior is as expected from the cyclic voltammetric observations. The decrease in \( \tau \) (form 4.22 sec to1.1 sec) with respect to increase in current (form 0.25 \( \mu \text{A} \) to2.5 \( \mu \text{A} \)) is presented in (figure-2.29). The plots of \( i \) vs \( 1/\tau^{1/2} \) is found to be linear and passing through the origin [plot 2.18]. This indicates that the process is diffusion controlled.

Figure-2.31 shows the comparison of three chronopotentiograms recorded at different current to illustrate the existence of two different species of Eu(III) in support to the cyclic voltammetric observations. From the plot of \( (\tau^{1/2} - t^{1/2}) / t^{1/2} vs E \) the electrode kinetics parameters like, \( \alpha_{na} \) (Transfer coefficient and standard heterogeneous rate constant \( k^0_{r, h} \)) are evaluated.
2.3.5. **Chronoamperometry of Eu(III) in aqueous medium.** The chronoamperograms of Eu(III) are recorded by applying constant potential in the range of $-0.3$ to $-0.9$ V in the case of cathodic process and $-0.5$ to $-0.9$ V in the case of anodic process in pH-2.5 NaCl-HCl medium. The flow of current is plotted exponential as a function of time. The plot $i$ vs $t^{1/2}$ is found linear in accordance with the Cottrel equation. From the slope of this plots, the diffusion coefficient of Eu(III) is calculated. This conform the Eu(III)/Eu(II) couple system is diffusion control.

2.3.6. **Chronocoulometry of Eu(III) in aqueous medium.** The chronocoulograms of Eu(III) is recorded by applying constant potential in the range of $-0.3$ to $-0.9$ V in the case of cathodic process and $-0.5$ to $-0.9$ V in the case of anodic process in pH-at pH-2.5(NaCl-HCl) medium. The flow of charge($q$) is found exponential as a function of time. The plot of $i$ vs $q^{1/2}$ is found linear in accordance with of Integration of Cottrel’s equation. This further conforms diffusion control nature of Eu(III)/Eu(II) couple. From the slop of the plot, the value of D (Diffusion coefficient) for Eu(III)/Eu(II) reaction calculated.
4.4. Reference.

1. H. J. Sand *Phil. Mag.*, 1 (1901) 45.