UNIT 8 POLAROGRAPHY AND AMPEROMETRIC TITRATIONS

Structure

8.1 INTRODUCTION

In the previous unit of this block, that is unit 7 of this Electroanalytical methods-III course we have discussed voltammetry. This unit is devoted to Polarography and Amperometric titrations. In this unit, the theory of Polarography and Amperometric titrations will be discussed, the applications of which have been discussed in detail in Unit 9 of this course.

In this unit, we will start our discussion with a typical polarogram and then the dropping mercury electrode (DME). After discussing in detail the advantages of a DME we will continue our discussions on limiting and migration current, followed by diffusion and residual current. The factors affecting residual current are then discussed. This is followed by the discussion on half wave potential, $E_{1/2}$ and effect on complexing agents on it. The determination of n and reversibility are discussed taking the log plot of Cd(II) in 1 M KCl. Discussion of kinetic currents, catalytic currents, adsorption waves, polarographic maxima and maximum suppressors are then done. Qualitative as well as quantitative polarographic analysis including calibration plot, internal standard method and method of standard addition are discussed. The discussion on polarography is concluded with the instrument involved in polarographic analysis. Then we discuss amperometric titrations where we start with the advantages of amperometry followed by a few examples of amperometric titrations.

Objectives

After studying this unit you should be able to:

- define polarography,
- discuss the details of a dropping mercury electrode,
- discuss the limiting and migration currents,
- discuss the diffusion and residual currents,
- discuss the factors affecting the diffusion current,
- give the details of the polarographic equation ,
- discuss the $E_{1/2}$ and effect of complexing agents,
- discuss the estimation of n-values and reversibility,
- discuss the currents other than the diffusion current,
- discuss the polarographic maxima and maximum suppressors,
- discuss the qualitative and quantitative polarographic analysis,
- discuss the instrument, and
- discuss the details of amperometric titrations

8.2 POLAROGRAPHY

The polarographic method of analysis was developed by Jaroslav Heyrovsky in 1922 which is the earliest voltammetric technique introduced. He received Nobel Prize in 1952 for developing this technique using dropping mercury electrode as the working electrode. He called the recorded current-potential curves as polarograms and introduced the term polarography.

According to Ilkovic equation, i_d is proportional to concentration keeping all other factors of the equation constant. So, if some of the electroactive material in the solution is removed by interaction with some other reagent (e.g. EDTA reagent for Zn^{2+} determination) the diffusion current will decrease. This is the fundamental principle of amperometric titrations or polarographic titrations.

Most metal ions are reducible at DME, and multicomponent mixtures can often be analysed by selecting an appropriate supporting electrolyte so that the half-wave potentials of the two ions are differed by about − 0.2 V vs SCE or by using complexing agents by taking the advantage of complexing ability of the metal ions. Based on this, polarography is used predominantly for trace metal analysis of alloys, ultra-pure metals, minerals/metallurgy, environmental analysis (air, water, soil and sea water contaminant), foodstuffs, beverages and body-fluids, toxicology and clinical analysis. Reducible anions such as BrO_3^-, IO_3^-, $Cr_2O_7^{2-}$ and NO_2^- can also be determined using well buffered solutions.

During electrolysis, chemical reactions occur under the influence of an electromotive force at electrodes immersed in solutions. The reactions occurring at the electrodes i.e. electrode reactions are characterized by the transfer of electrons between the electrode and the substances in the solution. Because of this the equality of positive and negative ions are unbalanced at the electrode but is counter acted by oppositely directed movement of positive and negative ions through the solution to produce the flow of current through the solution.

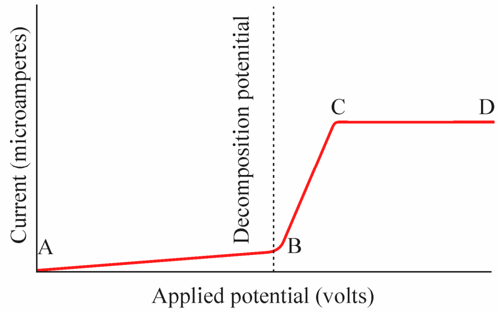

Fig. 8.1: A Typical Polarogram

This is the current which is actually measured by the movement of electrons in the external circuit connecting the two electrodes. Therefore, the current is the result of the electrode reaction. The electrode at which reduction occurs is the “cathode” and electrode at which oxidation occurs is the “anode”. The curve obtained by plotting e.m.f. applied to a cell against the resulting current is the current-voltage curve (Fig. 8.1).

When the applied potential is equal to the decomposition potential (B) of the electroactive substance (e.g. Zn^{2+}) at the cathode the current starts increasing due to the following cathodic reaction.

$$Zn^{2+} + 2e^- + Hg \leftrightarrow Zn\,(Hg)$$

The resulting zinc will form amalgam with mercury on the surface of the mercury electrode. As the potential of the dropping mercury electrode (micro electrode) is made more negative, there is a further increase in current in accordance with Ohm’s law and the concentration of Zn^{2+} is reduced at the electrode surface until at point C the concentration at electrode surface is negligibly small in comparison with that in the bulk of the solution. From C to D the current remains constant which is determined by the rate of diffusion of Zn^{2+} ions from the bulk of the solution to the electrode surface. The number of Zn^{2+} ions diffusing from the bulk of the solution to the electrode surface is equal to the number that is deposited when the steady state is reached or the rate of diffusion is equal to the rate of reduction.

When the applied e.m.f. exceed the decomposition potential the DME becomes depolarized as Zn^{2+} will become Zn (0) forming amalgam and there is a reversible electrode reaction. As long as the electrode is ideally depolarized, passage of current does not cause the potential to deviate from its reversible value and is determined by Nernst equation.

$$E = E^0 + \frac{0.059}{2}\log[Zn^{2+}] \qquad \text{… (8.1)}$$

At the point C the current no longer increases linearly with applied potential but approaches a steady limiting value at the point D; no increase in current is observed at higher cathode potential until a second compound able to depolarize the indicator electrode is present in the solution. So from the point C onwards the DME once again becomes depolarized. Because of this polarized and depolarized nature of the electrode that is caused by electrode reaction the curve so obtained is called as polarogram.

SAQ 1

What do you mean by

a) Polarogram

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b) Polarography

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8.3 THE DROPPING MERCURY ELECTRODE (DME)

DME: An electrode in which successive drops of mercury fall from a capillary tube due to gravity

This small polarizable electrode is produced by passing a stream of mercury through a resistance glass capillary having a very fine bore of 0.05–0.08 mm internal diameter and 5–9 cm long. The drops fall at a steady rate of 3–5 sec per drop and is adjusted under a head of 40–60 cm of mercury. The current oscillates between a near-zero value as drop falls from the capillary to a maximum value as the surface area of a new drop increases.

The dropping mercury electrode has several advantages:

i) Its surface area is reproducible with a given capillary

ii) The constant renewal of the electrode surface eliminates passivity or poisoning effects.

iii) The large hydrogen overpotential on mercury renders possible the deposition of substances difficult to reduce such as aluminium ion and manganese (II) ion (The current-potential curves of these ions are not accessible with platinum micro electrode).

iv) Mercury forms amalgams with many metals.

v) The diffusion current assumes a steady value immediately and is reproducible.

vi) The surface area of the electrode can be calculated from the weight of the drops.

The dropping mercury electrode therefore is useful over the range + 0.3 to − 2.0 V vs. SCE. Above + 0.4 V mercury dissolves and gives an anodic wave due to oxidation to mercury (I) ion. At potentials more negative than − 1.8 V vs SCE visible hydrogen evolution occurs in acid solutions and at − 2.0 V the supporting electrolytes of alkali salts begin to discharge.

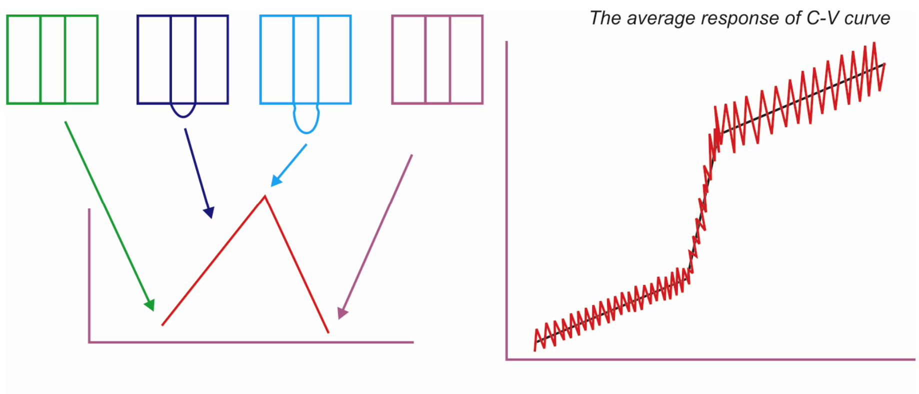

Fig. 8.2: Showing current oscillation with DME.

SAQ 2

a) What are the advantages of a DME?

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b) Write about polarographic maxima.

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c) Give the potential range of DME.

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8.4 MIGRATION AND LIMITING CURRENTS

8.4.1 The Limiting Current

The limiting current obtained with the dropping mercury electrode is caused by the extreme state of concentration polarization which results from the depletion of the concentration of the electro-reducible or electro-oxidizable substance at the electrode surface by the electrode reaction. The reducible or oxidizable ions are supplied to the depleted region at the electrode surface by two forces:

1. A diffusive force, proportional to the concentration gradient at the electrode surface.
2. An electrical force, proportional to the electrical potential difference between the surface and the solution.

So the limiting current is regarded as the sum of 'diffusion current' and a 'migration current'.

8.4.2 The Migration Current

The migration current is due to the migration of reducible or oxidizable ions which is proportional to the electrical potential gradient at the electrode due to attraction. Unless this potential gradient is removed the limiting current cannot be proportional to the concentration of electroactive ions in the solution. This migration current is usually eliminated by adding 50 or 100 fold excess of an inert supporting electrolyte. Commonly used supporting electrolytes are potassium or sodium salts. The potassium ions cannot be discharged at cathode until the impressed voltage becomes large. The large number of potassium ions therefore remain as a crowd around cathode and restrict the potential gradient to a region so very close to the electrode surface. So there is no longer an electrostatic attraction operative to attract other reducible ions from the bulk of the solution. Under these circumstances the limiting current is solely controlled by the diffusion of the electroactive species through the concentration gradient adjacent to the electrode

The migration current depends on the transference number of the reducible or oxidizable ion in the solution and the total limiting current.

$$i_m = T_i \, i_l \qquad \ldots (8.2)$$

Migration: Movement of cations or anions in response to an applied potential

Table 8.1 Limiting Current in solutions containing various concentrations of supporting electrolytes

(0.05 mM lead nitrate in potassium nitrate supporting electrolyte and 0.0004% sodium methyl red maximum suppressor)

KNO_3, M	Transference Number of Pb^{2+} ion	Limiting Current, μA
0.0	0.477	17.6
0.0002	0.430	15.0
0.0005	0.378	13.4
0.001	0.313	12.0
0.005	0.132	9.8
0.1	0.0089	8.45
1.0	0.00091	8.45

Table 8.1 clearly demonstrates the fact that the transference number of an ion decreased practically to zero in the presence of 100 fold excess of a supporting electrolyte. In such solutions almost all the current is carried through the cell by the potassium and nitrate ions. However, these are not reduced before the evolution of hydrogen and so the reduction of lead ions remains the only process by which electrons can be transferred across the interface between the electrode and the solution. In this way the migration current is practically eliminated by keeping the supporting electrolyte 50 to 100 times the concentration of reducible ion.

SAQ 3

a) What are the causes of migration current?

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b) How can the migration current be eliminated?

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8.5 DIFFUSION AND RESIDUAL CURRENTS

8.5.1 Diffusion Current

In the presence of excess supporting electrolyte the electrical force on the reducible/oxidizable ions is nullified and therefore, the limiting current is solely a diffusion current. Ilkovic (1934) examined the various factors which govern the diffusion current and deduced a theoretical equation as

$$i_d = 607\, n\, c D^{1/2} m^{2/3} t^{1/6} \qquad \ldots (8.3)$$

where i_d = average diffusion current in microamperes during the life of the drop

n = the number of electrons consumed in the reduction or oxidation of one mole of the electroactive species

D = diffusion coefficient of the reducible or oxidizable substance expressed as cm^2 /second

c = concentration of electroactive species in millimoles per dm^3

m = the rate of flow of mercury from the dropping mercury electrode expressed in mg/ second

t = drop time of mercury in seconds

The constant 607 is a combination of natural constants, including the Faraday. This is an important equation because it accounts for the linear dependence of i_d upon c keeping all other factors constant. It is useful in quantitative polarographic analysis.

In practice, the limiting current is not exactly the diffusion current. The supporting electrolyte which is 50 to 100 times that of electroactive substance contains impurities which may contribute a small current in addition to non-faradaic condenser current. This is known as 'Residual Current'.

8.5.2 Residual Current

Even in the absence of electroactive substance in the solution having only supporting electrolytes a small current is always present which is referred as residual current which consists of two components.

The first is reduction of trace impurities (faradaic current) present in the large concentration of supporting electrolyte used. These include dissolved oxygen, traces of metal ions such as ferric iron, lead and arsenic. Out of these, dissolved oxygen can be removed by passing pure nitrogen for 10 to 15 minutes before taking C-V curve.

The second source is charging current or capacitive current which is non-faradaic and is present whenever the working electrode potential changes. Mercury is unique in remaining electrically uncharged when it is dropping freely into the supporting electrolyte. The small current that is observed from supporting electrolyte solution is because of continuous charging of new mercury drop to the applied potential in order to remain neutral. The mercury is covered with an electrical double layer of positively and negatively charged ions of the electrolyte. The capacity of the double layer and hence the charging current vary depending on the potential which is imposed upon mercury.

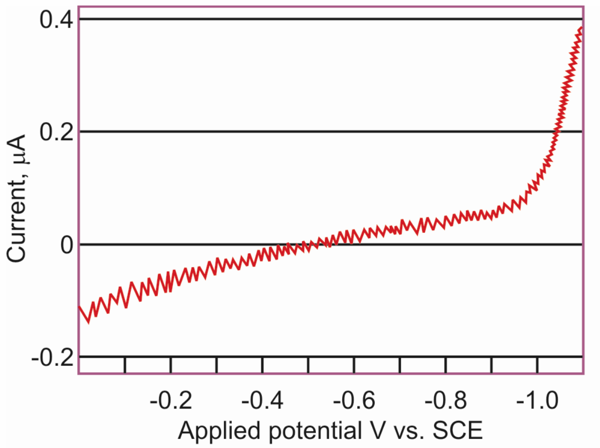

Fig. 8.3: Residual current for a 0.1 M solution of HCL

Supporting electrolyte: A large concentration of an inert electrolyte used to suppress migration current

The residual current is responsible for determining the accuracy and sensitivity of a polarographic method at low concentrations of electroactive substances below 10^{-4} M. At concentrations around 10^{-5}M of electroactive species the residual current is larger than the faradaic current of the substance to be determined and therefore not sensitive.

The residual current has to be compensated at the potential at which the diffusion current is measured.

SAQ 4

a) What do you mean by residual current?

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b) Distinguish between limiting current and diffusion current.

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8.6 FACTORS AFFECTING THE DIFFUSION CURRENT

The Ilkovic equation is important because it shows that there is a linear relationship between i_d and concentration of electroactive substance. It also accounts for many factors which influence the diffusion current and these factors are, the concentration of electroactive substance, the dimensions of the capillary and the pressure on the dropping mercury, temperature, the viscosity of the medium, the composition of the base electrolyte etc.

8.6.1 The Concentration of Electroactive Substance:

According to the Ilkovic equation,

$i_d = Kc$ or i_d/c is constant keeping all other factors constant.

This is the basis of quantitative polarographic analysis. But there are instances when i_d/c is not constant and the current is determined by rate of chemical reaction (kinetic/ catalytic currents) and some times the adsorption of electroactive substance or its electrode reaction product (adsorption waves).

8.6.2 The Capillary Characteristics and the Factors Affecting Them

From the Ilkovic equation it is seen that the diffusion current depends on m and t (together referred as capillary characteristics) and are therefore affected by their variations. '*m*' is directly proportional and '*t*' is inversely proportional to the net pressure on the mercury drop. These effects are reported in terms of height of mercury column above the capillary tip. Accordingly, $m^{2/3}\, t^{1/6}$ is proportional to $\sqrt{h_{corr}}$ and i_d of the Ilkovic equation.

$$i_d / \sqrt{h} = K \text{ where } K \text{ is constant}$$

$$i_d = K'(m^{2/3} t^{1/6}), \text{ where } K' = 607\, nD^{1/2} c$$

$$m \,\alpha\, h$$

$$t \,\alpha\, \frac{1}{h}$$

$$i_d = K'\left(h^{2/3} \times h^{-1/6}\right) = K'\left(h^{\frac{2}{3}-\frac{1}{6}}\right) \qquad \ldots (8.4)$$

$$= K'\left(h^{\frac{4-1}{6}}\right) = K' h^{\frac{1}{2}}$$

$$\frac{i_d}{\sqrt{h}} = K'$$

Any deviation from this indicates that the current must be partly or wholly governed by the rate of some process other than the diffusion of electroactive substance to the electrode surface.

Table 8.2: Effect of mercury pressure on 'm' and 't':

(Solution: 0.10M potassium nitrate, data secured at -1.0 V vs SCE)

h_{Hg}, cm	m, mg/sec	t, sec	mt, mg	hcorr, cm
100.8	4.2730	1.751	7.48	106.20
81.0	3.1837	2.346	7.47	79.20
58.0	2.2645	3.290	7.45	56.20
43.0	1.6625	4.505	7.49	41.20
32.0	1.2155	6.145	7.47	30.20
27.0	1.0118	7.372	7.46	25.20
Mean	-	-	7.47 ± 0.01	

8.6.3 Temperature

The change in temperature affects all values in the Ilkovic equation except the value of 'n'. The temperature coefficient of 'm' is about +0.27% per degree, while that of 't' is about – 0.22% per degree. So the temperature coefficient $m^{2/3}\, t^{1/6}$ is about +0.15% per degree. The temperature coefficient of the equivalent conductance and thereby the diffusion coefficient is close to +0.02 per degree and of C for aqueous solutions –0.00025 per degree. In addition, the numerical constants 607 is also affected and the temperature coefficient of this constant K is +0.00012 per degree. Combining all these values gives the temperature coefficient of the diffusion current as +0.013 per degree. So the diffusion current increases about 1.3% per one degree rise in temperature. Therefore, it is advisable to keep the temperature constant within $\pm$ 0.5^o.

8.6.4 The Solvent and the Supporting Electrolyte

The diffusion current depends on 'D' of the electroactive species which in turn depends on the viscosity of the solution. 'i_d' decreases with increase in the viscosity of the solution as D is inversely proportional to the viscosity, η of the medium. According to Ilkovic equation, therefore i_d is proportional to $\eta^{1/2}$. η varies as the aqueous solution changed partly to non-aqueous medium using solvents such as methanol, dioxane etc.

Changes in the composition of the supporting electrolyte by adding complexing ligands to the electrolyte solution changes the size of the metal complex and therefore D of the ion. i_d therefore decreases with complexation and $E_{1/2}$ shifts to more negative potentials.

It is necessary to keep the concentration of every constituent of the supporting electrolyte constant within about $\pm$ 10% to ensure the variation of i_d resulting from this effect (viscosity) will be negligibly small.

SAQ 5

a) What is referred to as capillary characteristics and what are the factors affecting them?

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b) In what range should the temperature be kept during polarographic experiment and why?

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8.7 POLAROGRAPHIC EQUATION

Let us take a general electrode reaction in which any process of reduction at the cathode is accompanied by a simultaneous oxidation as free electrons cannot exist in solution.

$$\mathrm{Ox} + n\mathrm{e} \leftrightarrow \mathrm{Red}$$

The electrode potential for such reversible reaction is given by

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \qquad \ldots (8.5)$$

a_{ox} and a_{red} are the activities of the oxidant and the reductant respectively as they exist at the electrode-solution interface (denoted by the subscript 'o' in Eq. 8.1). By substituting all constants the equation becomes

$$E = E^0 + \frac{0.059}{n}\log\frac{[\mathrm{Ox}]_0}{[\mathrm{Red}]_0} \qquad \ldots (8.6)$$

Before the commencement of the polarographic wave only a small residual current flows and the concentration of electroactive material is same in the entire solution. As soon as the applied e.m.f. exceeds the decomposition potential of the electroactive material, some of the reducible substance at the electrode-solution interface is reduced and its concentration begins to decrease. Since there is a concentration gradient between the concentration of the substance at the interface and the bulk of the solution some ions will move in from the bulk of the solution to the interface by means of diffusion. The current observed depends upon the rate of the diffusion of oxidant and is given by

$$i = K_1([\mathrm{Ox}] - [\mathrm{Ox}]_0) \qquad \ldots (8.7)$$

so that according to Ilkovic equation K_1 is equal to $607\, n_{\mathrm{ox}} D_{\mathrm{ox}}{}^{1/2} m^{2/3} t^{1/6}$.

When the current attains the limiting value represented by the diffusion current plateau the concentration of oxidant at the electrode-solution interface will be essentially zero, as it is reduced as soon as it reached the interface from the bulk of the solution. The current therefore is i_{d} and Eq. 8.7 may be written as,

$$i = K_1[\mathrm{Ox}] = i_{\mathrm{d}} \qquad \ldots (8.8)$$

From Eq. (8.7) & (8.8) it follows that

$$[\mathrm{Ox}]_0 = (i_{\mathrm{d}} - i)/K_1 \qquad \ldots (8.9)$$

If the metal ion (oxidant) is reduced to metal (reductant), most of the reductant will form amalgam with the dropping mercury electrode, then the concentration of the metal in the amalgam is also directly proportional to the current on the wave. Therefore, the concentration of reductant formed is proportional to the observed current, so

$$i = K_2[\mathrm{Red}]_{\mathrm{o}} \qquad \ldots (8.10)$$

where $K_2 = 607\, n_{\mathrm{red}} D_{\mathrm{red}}{}^{1/2} m^{2/3} t^{1/6}$

If the reductant is soluble in water, it will diffuse from the surface of the electrode to the bulk of the solution. So, the concentration of $[\mathrm{Red}]_{\mathrm{o}}$ at the surface at any value of 'i' will be proportional to the rate of diffusion of the reductant from the surface of the electrode to the solution (under the concentration gradient $[\mathrm{Red}]_{\mathrm{o}}$) and hence the same Eq. (8.10) also holds good.

Substituting these in Eq. (8.6)

$$E = E^0 - \frac{0.059}{n}\log\frac{K_1}{K_2} - \frac{0.059}{n}\log\frac{i}{i_{\mathrm{d}} - i} \qquad \ldots (8.11)$$

when the potential of the dropping electrode is equal to the half- wave potential, $E_{1/2}$ where $i = i_{\mathrm{d}}/2$ the last term in the Eq. (8.11) then becomes zero and we have,

$$E = E_{1/2} = E^0 - \frac{0.059}{n}\log\frac{K_1}{K_2} \qquad \ldots (8.12)$$

Eq. (8.11) may now be written as,

$$E = E_{1/2} - \frac{0.059}{n}\log\frac{i}{(i_{\mathrm{d}} - i)} \qquad \ldots (8.13)$$

This equation is termed as "Equation of the Polarographic Wave" and represents the potential as a function of current at any point on the polarographic wave. The theoretical treatment for anodic waves is similar to the above.

SAQ 6

What is the polarographic equation and what does it represent?

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8.8 $E_{1/2}$ AND EFFECT OF COMPLEXING AGENTS

8.8.1 Half-wave Potential, $E_{1/2}$

The electro-active material in polarography is characterized by its half-wave potential, $E_{1/2}$. Under any defined set of experimental conditions, each substance has its own characteristic $E_{1/2}$ and this is the basis of qualitative polarographic analysis. The half-wave potential is defined as the potential at which the current due to the reduction or oxidation of the substance responsible for the wave is half as large as on the plateau (Fig. 8.4a and 8.4b).

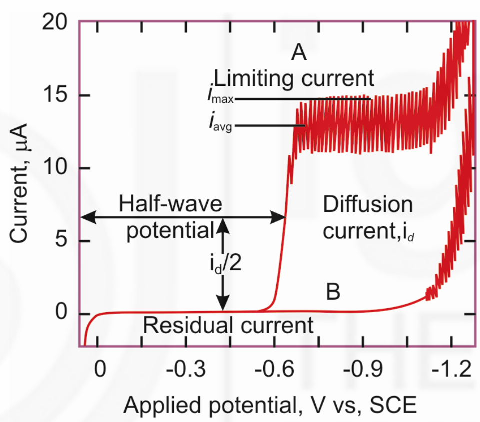

Fig. 8.4a: Polarogram A is 0.5mM Cd(II) in 1M HCl
Polarogram B is 1M HCl, supporting electrolyte

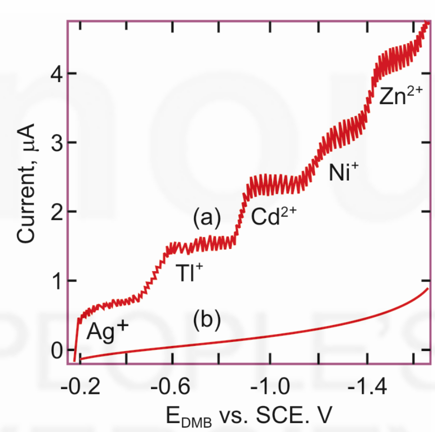

Fig. 8.4b: Polarogram a is multiple metal ions in 1 M NH_3 and 1M NH_4Cl
Polarogram b is 1 M NH_3 and 1M NH_4Cl, supporting electrolyte

The half-wave potential is also independent of the electrode characteristics and concentration of the electroactive substance, therefore serves for the qualitative identification of an unknown substance.

8.8.2 Effect of Complexing Agents

In case of complexation of metal ion with the complexing agent the electrode reaction proceeds in two steps

$$MX_p^{(n\text{-}pb)+} \leftrightarrow M^{n+} + pX^{-b} \qquad \text{... (8.14)}$$

$$M^{n+} + ne^- + Hg \rightleftharpoons M\,(Hg) \qquad \text{... (8.15)}$$

and $E_{1/2}$ of the metal ion is shifted to more negative value compared to the reduction of simple metal ion in the non-complexing medium. The expression for the electrode potential for such system is given as

$$(E_{1/2}) = E^{o} + \frac{0.05915}{n}\log K_{\text{instab}} - \frac{0.05915}{n}\log[X^{b-}]^{p} \qquad \ldots (8.16)$$

where p is the co-ordination number of the complex formed and X^{b-} is the complexing agent. p is determined by taking $E_{1/2}$ values with varying concentrations of complexing agent.

$$(E_{1/2})_{b} - (E_{1/2})_{\text{simple}} = \frac{0.05915}{n}\log K_{\text{instab}} - p\,\frac{0.05915}{n}\log[X^{b-}] \qquad \ldots (8.17)$$

If a graph is drawn between log[X] and $E_{1/2}$ (Fig.8.5) a line with the slope equivalent to $[-p\,\frac{0.05915}{n}]$ will be obtained from which

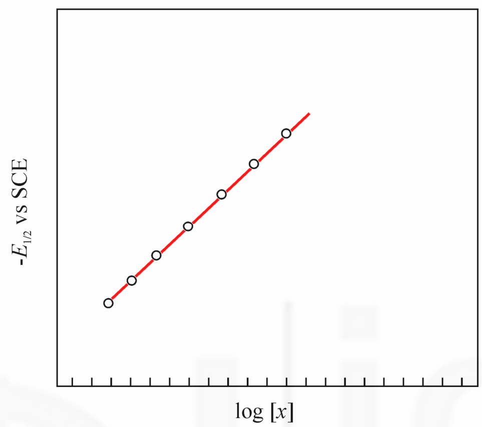

Fig. 8.5: Log plot

'p' is determined. Once p is known the instability constant of the complex ion is determined using the Eq. (8.17). The shift of $E_{1/2}$ of metal ion by complexation is useful for quantitative analysis of samples containing more than one metal ion to eliminate interfering effect of one metal ion upon another or promote separation of $E_{1/2}$ of metal ions in a mixture for simultaneous determinations.

Table 8.3: $E_{1/2}$ values of few metal ions in complexing and non-complexing medium at DME

Ion	Non-complexing media	1M HCl	1M KCN	1M NH_3, NH_4Cl
Cd^{2+}	–0.59	–1.18	–0.64	–0.81
Pb^{2+}	–0.40	–0.72	–0.44	–0.67
Cu^{2+}	+0.02	NR	+0.04	–0.24
			–0.22	–0.51
Ni^{2+}	---	–1.36	–1.20	–1.10
Co^{2+}	---	–1.45	–1.20	–1.29

8.9 DETERMINATION OF 'n' AND REVERSIBILITY

It follows from the Eq. (8.13) when a plot of log ($i/i_d - i$) is plotted against the corresponding potential of the electrode on the raising portion of the wave, a straight line will be obtained. The slope of this line will be equal to 0.05915/n from which 'n' can be determined. If 'n' is an integer value we can conclude that the electrode reaction responsible for this wave is reversible. If the slope of log plot is larger than the expected or 'n' is not integer value then the wave is irreversible or is a proof of the existence of some slow step in the over-all electrode reaction. In such cases the waves are more drawn–out than reversible waves, and the equation is

$$\mathrm{Ox} + ne^- \rightarrow \mathrm{Red}$$

The half-wave potential, $E_{1/2}$ for reversible wave is easily found from a log plot by interpolation to find the value of the potential when the log term is zero (Fig.8.6).

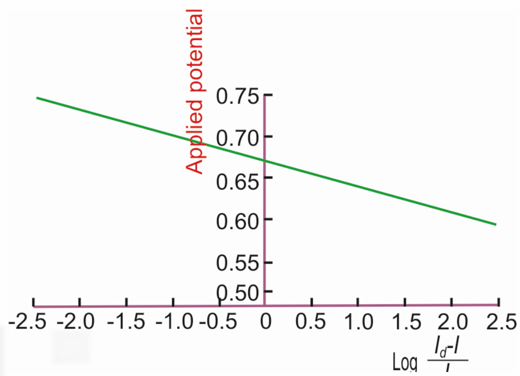

Fig. 705: log plot of Cd(II) in 1M KCl

Another method to determine the reversibility of electrode reaction which is very simple and rapid is measuring the potential corresponding to ¼ and ¾ from the polarogram.

At $E_{1/4}$ for a reversible cathodic wave

$$E_{1/4} = E_{1/2} - \frac{0.05915}{n} \log \frac{i_d/4}{i_d - i_d/4}$$

$$= E_{1/2} - \frac{0.05915}{n} \log \frac{1}{3}$$

and

$$E_{3/4} = E_{1/2} - \frac{0.05915}{n} \log 3$$

so that

$$E_{3/4} - E_{1/4} = -\frac{0.05915}{n} \log 9 = -\frac{0.0564}{n}$$

Therefore, the value of $E_{3/4}$ - $E_{1/4}$ is equal to $-\frac{56.4}{n}$ mV and for reversible anodic wave it is equivalent to $+\frac{56.4}{n}$ mV.

Irreversible reactions:

Many electrode reactions are partially or totally irreversible

$$\mathrm{O} + ne^- \rightarrow \mathrm{R}$$

The polarogram obtained in such cases is a drawn-out and less well defined. The polarographic equation for such reaction is

$$E = E_{1/2} - \frac{0.05915}{\alpha n} \log \frac{i}{i_d - i} \quad \ldots (8.18)$$

where α is transfer coefficient and accounts for the kinetics of the electrode process.

Even in such electrode processes diffusion current is proportional to concentration and therefore, can be used for quantitative analysis. However, $E_{1/2}$ slightly varies with concentration of electro-active substance in the solution.

SAQ 7

How can you determine whether a reaction is reversible or not with the help of "Equation of the polarographic wave"?

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8.10 CURRENTS OTHER THAN DIFFUSION CURRENT

These include kinetic currents, catalytic currents and adsorption waves.

8.10.1 Kinetic Currents

Some substances are not electroactive but made electroactive on chemical reactions. The product so formed by chemical reactions undergoes reduction or oxidation at DME. The height of the polarographic wave or current is determined by the rate of the chemical reaction that produces an electroactive substance in thin layer of the solution around the mercury drop. The waves of this kind are referred as kinetic waves and the mechanism responsible for them may be written as

$$Y \underset{K_b}{\overset{K_f}{\rightleftharpoons}} O \quad \text{'Y' is not electroactive but 'O' is}$$

$$O + ne^- = R \quad \ldots (8.19)$$

where K_f and K_b are first order rate constants (in sec^{-1}) for the forward and backward reactions.

Example: Diol does not undergo reaction at DME but on conversion to aldehydo form is reducible and the wave height reflects the rate of transformation of diol to aldehydo form.

The kinetic current obtained is given as

$$i_k = 493 n D^{1/2} c_y m^{2/3} t^{2/3} (K_f / K_b^{1/2}) \quad \ldots (8.20)$$

where i_k is the average kinetic current during the life of the drop and D is the diffusion coefficient of Y or O.

The kinetic currents are recognized from $m^{2/3}\, t^{2/3}$ which does not vary with height of the mercury column above the capillary and is independent of h_{corr}.

The kinetic currents are not in much use in practical quantitative analysis because of poorer sensitivity than i_d. Also there is a possibility of impurities present in solution which may alter the height of a kinetic wave by catalyzing rate-determining step.

8.10.2 Catalytic Currents

When electroactive substance is reduced at the electrode by normal process

$$O + ne^- = R \qquad \ldots (8.21)$$

and if the solution contained another substance, Z which is not electroactive or reduces at more negative potential than 'O', it may catalyze the back reaction and the reagent O is produced by the following mechanism

$$R + Z \xrightarrow{k_f} O \qquad \ldots (8.22)$$

Because of the regeneration of electroactive substance, more and more 'O' is reduced at DME and there is an increase in current i.e. catalytic current. This process is continued until the applied potential is very much negative corresponding to the limiting plateau of 'O'. The average catalytic current over the life of a drop is

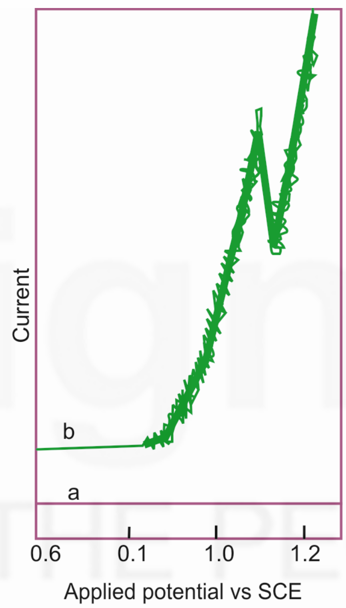

Fig. 8.7: Polarographic Catalytic curve of Te (IV)
a) 0.005 ppm Te (IV) in sodium tartarate medium.
b) A + KIO_3 as oxidant

given by $$I_c = 493\, n\, D_0^{1/2} c_0 m^{2/3} t^{2/3} [(k_f + k_b)\, c_z^{\,0}]^{1/2} \qquad (8.23)$$

Example: $V(V) + e^- \rightarrow V(IV)$. If the solution contains a small amount of hydrogen peroxide V(V) is regenerated by oxidation of V (IV). 8×10^{-7} M V (V) in 0.1 M phosphate buffer at pH 4.9 gives a current which is few thousandths of microampere. But the same concentration of V(V) in the presence of 0.007 M hydrogen peroxide gives 18.6 microamperes of current.

It is therefore, of importance for determining exceedingly low concentrations of original electroactive substance. Therefore, the catalytic currents are highly useful for trace analysis of number of transition metal ions such as tungstate, vanadate, molybdate, titanium(IV), Te(IV) and Iron(III) with oxidizing agents like nitrate, hydrogen peroxide, chlorate, perchlorate, KIO_3 and hydroxylamine because i_c is proportional to the concentration of electroactive substance (O).

The catalytic currents are identified as I_c is independent of h_{corr} like kinetic currents.

8.10.3 Adsorption Waves

Some electroactive species or their products due to electrooxidation or reduction are adsorbed on the surface of mercury drop and give adsorption waves. In electrode reaction

$$O + ne^- \rightarrow R \qquad \ldots (8.24)$$

if 'R' is adsorbed, the current obtained is small (adsorption wave) and a single wave is obtained whose height is proportional to 'O'. But after certain concentrations when the surface of the drop is saturated with 'R', a second wave is observed at more negative potential which is the 'normal wave'. This normal wave represents the reduction of 'O' to dissolved 'R'.

From the time the normal wave appeared, the height of the adsorption wave remains constant. The total wave of first and second together is proportional to the concentration of 'O' and is diffusion controlled.

If 'O' is adsorbed and not 'R', the normal wave appears on the positive side of the adsorption wave.

Adsorption waves are observed in solutions of thiols, certain organic mercurials, uracils, arsenic (III) etc.

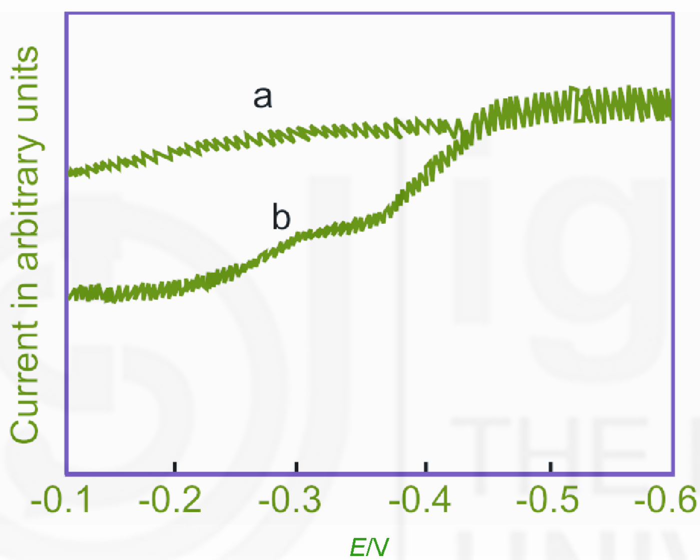

Fig. 8.8 Polarogram of sodium propyl xanthate

(a) 0.2 M NH_4Cl, pH 6. 5
(b) a + 1.2 mM sodium propyl xanthate (adsorption + normal wave)

These adsorption waves have been used to evaluate the area of adsorbed species using the equation given below when only adsorption is seen without normal wave.

$$i_a = 13.66\, nm^{\frac{2}{3}} t^{\frac{-1}{3}} / A \qquad \ldots (8.24)$$

where 'A' is the area (in Å) covered by each adsorbed molecule.

SAQ 8

What gives rise to adsorption waves?

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8.11 POLAROGRAPHIC MAXIMA: MAXIMUM SUPPRESSORS

Current–voltage curves obtained with electro-reducible ions at DME are frequently distorted by increasing the current beyond the diffusion current value and rapidly decrease to the normal diffusion plateau after a critical value is reached as the applied potential is increased. This abnormal increase in current is referred as maxima and vary in shape from sharp peaks to rounded humps. To measure the true diffusion currents the maximum must be eliminated. This can be done by adding small amount of surface-active agents such as gelatin, dye stuff, Triton X-100 etc. which are likely to form an adsorbed layer on the mercury–solution interface to prevent streaming movement of the diffusion layer at the interface.

Gelatin is widely used in the concentration range of 0.002 to 0.01%. Higher concentration will suppress the diffusion currents also. Others frequently used are, Triton X-100 (a non-ionic detergent) in the range of 0.002 to 0.004% and methyl cellulose (0.005%).

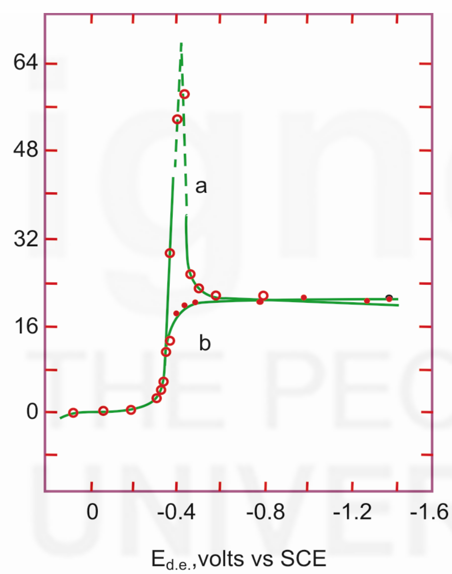

Fig. 8.9: Polarogram of 2.3 mM lead (II) in 0.1 M Potassium Chloride

a) In absence of a maximum suppresser

b) After addition of 0.0002% sodium methyl red.

8.12 QUALITATIVE AND QUANTITATIVE POLAROGRAPHIC ANALYSIS

The qualitative analysis of a sample is carried out by matching its $E_{1/2}$ with the tabulated values of the ions (given in the text books) in the supporting electrolytes used. It is also advisable to use the log-plot for knowing the correct $E_{1/2}$.

Table 8.4: The half-wave potentials of some of the common ions

Metal ion	Supp. electrolytes	$E_{1/2}$, V vs. SCE
	i)1 M NH_3 + 1 M NH_4 Cl	
Cd(II)		−0.81
Co(II)		−1.29
Cu(II)		−0.24
Fe(II)		−0.34 and −1.49
Mn(II)		−1.66
Mo(VI)		−1.71
Ni(II)		−1.10
Pb(II)		−0.67
Pd(II)		−0.75
Se(II)		−1.53
Te(IV)		−1.21
Tl(I)		−0.48
U(VI)		−0.8 and 1.4
	ii) 2 M HOAc and 2 M NH_4OAc, 0.01% Gelatin	
(ii)		
Cd(II)		−0.653
Co(II)		−1.19
Cu(II)		−0.07
Fe(II)		NR
Mo(VI)		−0.61 and 1.2
Ni(II)		−1.1
Pb(II)		−0.5
Pd(II)		−0.6
Se(II)		−1.11
Te(IV)		−1.18
Tl(I)		−0.47
U(VI)		−0.12
Zn(II)		−1.1
	0.1 M KCl, LiCl, $(CH_3)_4NCl$ or NH_4Cl	
(iii)		
Cd(II)		−0.60
Co(II)		−1.20
Cu(II)		> 0
Fe(II)		−1.3
Ni(II)		−1.1
Pb(II)		−0.4

Se(II)	NR
Te(IV)	−1.1 and 1.45
Tl(I)	−0.46
U(VI)	−0.185
Zn(II)	−0.995

$E_{1/2}$ of some anions

iv) Anion	Supporting Electrolyte	$E_{1/2}$, V vs. SCE
Br^-	$^-$0.1 M KNO_3	0.12
Cl^-	,,	0.25
I^-	,,	–0.03
CN^-	0.1 M NaoH	–0.36
IO_3^-	0.1 M Phosphate buffer, pH 6.4	–0.79
NO_2^-	2M Citrate, pH 2.5	–1.06
S^-	0.1M NaOH	–0.43
SCN^-	0.5 M KNO_3	0.10
$S_2O_3^-$	0.2M NaOAc, pH 5	– 0.40

(NR= not reduced)

Quantitative polarographic analysis:

Polarographic analysis can be used between 10^{-3} to 10^{-5} M concentrations of electroactive substances. If solutions have more than one electroactive substance and if their half-wave potentials in a particular supporting electrolyte differ by about 0.4 V for single charged ions and 0.2 V for doubly charged ions they can be determined.

If the half-wave potential of two ions are close then various experimental devices can be employed. They include

i) precipitation of one (eg. Lead and Zinc mixture – lead may be removed as lead sulphate precipitate for the determination of zinc).

ii) Complexation: By adding complexing agent, $E_{1/2}$ of one of the ions may be shifted to more negative potential thereby $\Delta E_{1/2}$ of ions becomes more. (eg.: Cu(II) ion can be complexed by potassium cyanide and thereby $E_{1/2}$ is shifted to more negative potential than lead or cadmium).

There are three methods which have been widely used in practice. In all these methods oxygen is removed before taking polarograms of solutions.

1. Wave height – Concentration plots (calibration/working plots)

Standard solutions of different concentrations of ions under investigation are prepared using the same supporting electrolyte and 0.005% maximum suppresser (say gelatin) and polarograms are drawn with the known concentrations of ions. Wave heights of all known concentrations are noted down and after making correction for residual current a plot is drawn as function of concentration (calibration curve). Keeping the supporting electrolyte and gelatin as above, polarogram of unknown is also recorded keeping temperature constant at 25°C. The wave height of this unknown is referred to the working curve and its concentrations is noted

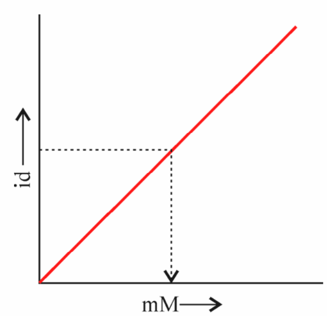

Fig. 8.10: Calibration plot

2. Internal standard (pilot ion) method

Polarogram of the unknown solution in a supporting electrolyte and gelatin is recorded and to the same solution a standard or pilot ion is added in known amount and current–voltage curve is recorded. The only condition is that $\Delta E_{1/2}$ of pilot ion and unknown should be differed by 0.4 V. The ratio of these two waves is compared with the ratios of known amounts of the two ions previously determined.

3. Method of standard addition

The polarogram of the unknown is first recorded and then a known amount of standard solution of the same ion is added and a second polarogram is taken. The calculations are made as below.

If i_{d_1} is the wave height the first polarogram of unknown solution of volume *V* and of concentration, c_u and i_{d_2} is the wave height of second polarogram after adding v cm^3 of standard solution of concentration c_s, then according to Ilkovic equation:

$$i_{d_1} = \mathrm{k}c_u$$

and

$$i_{d_2} = k(Vc_u + \mathrm{v}c_S)/(V+v)$$

thus $k = i_{d_2}(V+v)/(Vc_u + vc_S)$

therefore $$c_u = \frac{i_{d_1} vc_S}{(i_{d_2} - i_{d_1})(V+v) + i_{d_1} v}$$

… (8.26)

Concentration of unknown, c_u is therefore calculated. This procedure is sometimes reported as spiking used in environmental analysis.

SAQ 9

Give reasons for the addition of a small concentration of a surface active substance during the measurement of true diffusion current.

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8.13 INSTRUMENT

The basic apparatus for polarographic analysis is given in Fig. 8.11. The commonly used polarographic cell has an external reference electrode and is the H-cell. It consists of two compartments, one containing the solution to be studied and the other containing reference electrode. These compartments are separated by a cross-member filled with 4% agar-saturated potassium chloride gel, which held in place by a medium–porosity sintered disc. The second compartment is the solution compartment into which DME is inserted and this has N_2 inlet and outlet provision.

This simple recording polarogram unit has a potentiometer, 'P' by which any emf upto 3 Volts may be gradually applied to the cell. 'R' is a pen recorder and 'V' is voltmeter.

(Photo of Original Polarograph used by Heyrovsky obtained from Institute of Physical Chemistry, Praha, Czech-Republic is given below).

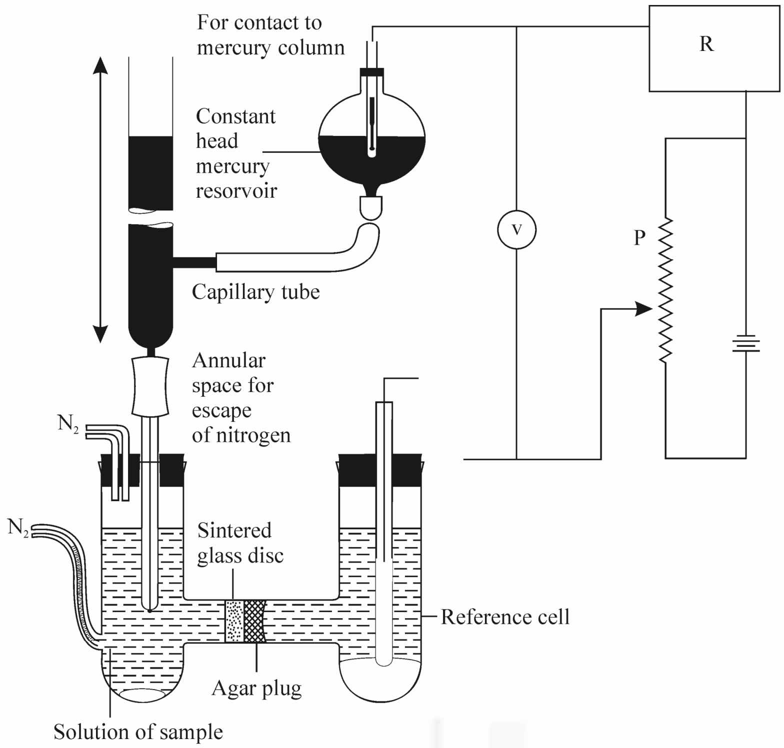

Fig.8.11: Apparatus for Polarographic analysis

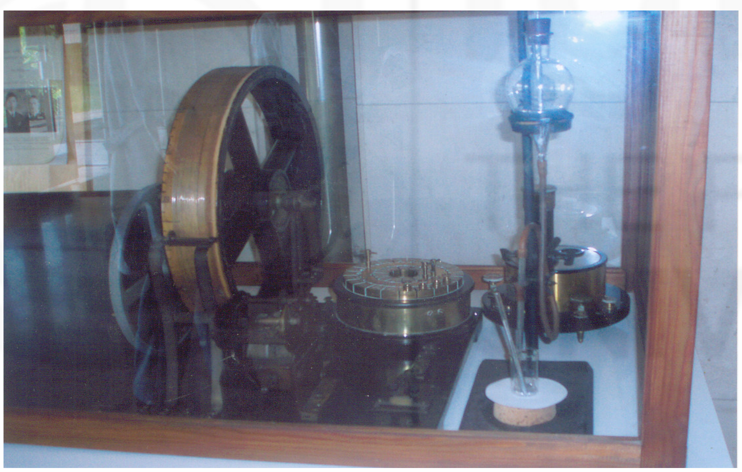

Fig. 8.12: Photo of Original Polarograph

SAQ 10

Draw the basic apparatus for polarographic analysis.

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8.14 AMPEROMETRIC TITRATIONS

According to Ilkovic equation i_d is proportional to concentration keeping all other factors of the equation constant. So, if some of the electroactive material in the solution is removed by interaction with some other reagent (e.g.: EDTA reagent for Zn^{2+} determination) the diffusion current will decrease proportionally.

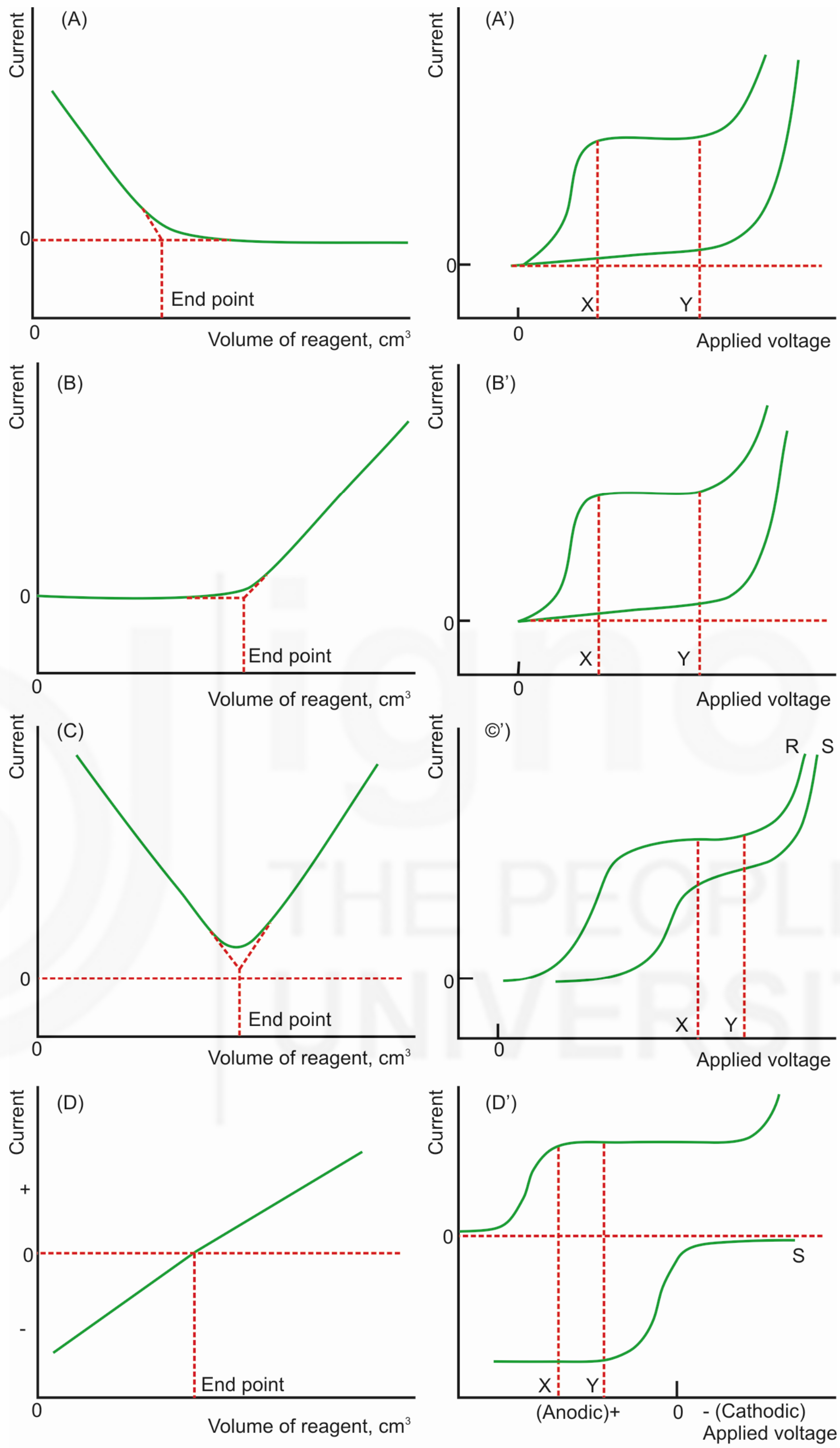

Fig. 8.13: A-D Common types of curves of amperometric titrations A′–D′ polarograms of individual substances (substance 'S' and reagent 'R')

This is the fundamental principal of amperometric titrations or polarographic titrations. The diffusion current at an appropriate applied voltage is measured as a function of the volume of the titrating solution. The end point is the intersection of two lines giving the change of current before and after the equivalence point.

The voltage applied at the beginning of the titration must be selected so that the diffusion current of the substance to be titrated or of the reagent or of the both, is obtained. Depending on the selection of the applied voltage between DME and reference electrode various types of titration curves are obtained as shown in Fig. 8.13.

For each titration the applied voltage is selected to the value between X and Y as shown in figures. A′ to D′ (S is the substance to be determined and R the reagent).

Fig 8.13 (A). Electroactive material is being removed from the solution by precipitation or complex formation with an inactive titrant at that potential applied. e.g. Pb^{+2} vs Oxalate or Zn^{2+} vs EDTA.

Fig. 8.13 (B). Substance to be determined does not give diffusion current but the titrant (reagent) gives current at the applied potential. (e.g: SO_4^{2-} ions titrated with Pb^{2+} ions). As long as the substance is available to the titrant, that titrant reacts with substance and current remains zero. After the substance is completely removed by reagent the excess reagent gives its diffusion current in proportional to the excess volume added. So, the reverse L shaped curve obtained.

Fig. 8.13 (C). Both substance to be determined and the titrating reagent give diffusion currents at the potential selected (eg. Pb^{2+} titrated with $Cr_2O_7^{2-}$).

Fig. 8.13 (D) At the applied potential substance gives anodic current and titrant cathodic current. (eg. I^- ion with $Hg(NO_3)_2$)

The titration cell is of Pyrex glass, that is a three necked, flat–bottomed flask into which a micro burette, dropping mercury that is a electrode, gas outlet tube for N_2 with an additional inlet N_2 provision. The cell is connected to a reference electrode in the form of an attachment with a sintered glass disc separating the titration cell and the RE.

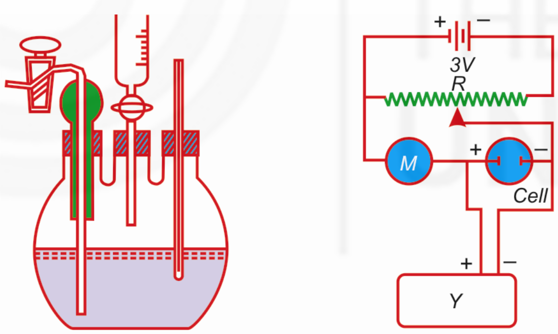

Fig. 8.14: a) Titration Cell b) Simple Polarograph Unit

The general procedure is as follows:
A known volume of the solution for estimation is placed in the titration cell, required amount of supporting electrolyte is added and the cell is connected to the terminals of the instrument. Dissolved oxygen is expelled by passing pure nitrogen gas for 10–15 minutes and initial current is noted. The known volume of the reagent is added from a microburette, N_2 is passed for 2 minutes and then stopped. The current and burette readings are both noted. This procedure is repeated until sufficient readings are obtained and the graph obtained gives end point at the intersection.

8.14.1 Advantages of Amperometry

1. The titration can usually be carried out rapidly, since the end point is found graphically; a few current measurements at constant applied voltage before and after the end point are sufficient.

2. Titrations can be carried out in cases in which the solubility relations are such that potentiometric or visual indicator methods are unsatisfactory. For example, when the reaction product is markedly soluble (precipitation titration) or appreciably hydrolysed (acid-base titration). This is because the readings near the equivalence point have no special significance in amperometric titrations. Readings are recorded in regions where there is excess of titrant, or of reagent, at which points the solubility or hydrolysis is suppressed by the Mass Action effect; the point of intersection of these lines gives the equivalence point.

3. A number of amperometric titrations can be carried out at dilutions (ca 10^{-4} M) at which many visual or potentiometric titrations no longer yield accurate results.

4. 'Foreign' salts may frequently be present without interference and are, indeed, usually added as the supporting electrolyte in order to eliminate the migration current which is not possible in case of conductometric titration.

5. The results of the titration are independent of the characteristics of the capillary.

6. The temperature need not be known provided it is kept constant during the titration.

7. Although a polarograph is convenient as a means of applying the voltage to the cell, its use is not essential in amperometric titrations. The constant applied voltage may be obtained with a simple potentiometric device.

8.14.2 Few Examples of Amperometric Titration

1. Determination of Zinc with EDTA

   Reagents required

   i) 0.005 M zinc ion solution

   ii) 0.01 M EDTA solution

   iii) Cyclohydoxylamine

   The titrant should be lean 10 times strong than the ion taken in the cell. Procedure: Place 5.00 cm^3 of zinc ion solution in the titration cell, add 1.0 cm^3 of cyclohexylamine and 19.0 cm^3 of distilled water, set the applied potential at −1.4 V vs SCE corresponding to Zn^{2+} . Deaerate the solution and titrate with standard EDTA solution. Pass N_2 for 1 minute then take readings of both burette and the galvanometer. Large initial current will be decreased as the titration proceeds to a very small value at the equivalence point and remains constant beyond the equivalence point. Use volume correction and plot the readings. The graph is as shown in the titration curve (Fig.8.13A). (1 ml of 0.01 M EDTA of Zn = 0.0006537 g of Zn.)

2. Determination of SO_4^{2-} with $Pb(NO_3)_2$ solution.
   At the potential applied −1.2 V vs SCE only Pb^{2+} is reduced to give diffusion current and is used as a titrant.

   Reagents required: 0.01 M AR K_2SO_4 and 0.1M lead nitrate solution, ethyl alcohol, conc. HNO_3 and thymol blue indicator solution.

Procedure: Take 25 cm^3 of potassium sulphate into the titration cell, add 2 to 3 drops of thymol blue indicator and few drops of conc. HNO_3 until a red color is obtained (pH is 1.2). To this add 25 cm^3 of ethyl alcohol which will reduce the solubility of $PbSO_4$ precipitate formed. The reaction is

$$K_2SO_4 + Pb(NO_3)_2 = PbSO_4 \downarrow + 2KNO_3 \quad \ldots (8.27)$$

Pass N_2 gas for 15 minutes to remove dissolved O_2 and connect the DME and RE to the respective terminals of the polarograph. Titrate with lead nitrate solution adding in small volumes and pure N_2 for 1 minute after each addition. Note down readings of burette and galvanometer after stopping the passage of N_2. Draw the graph between volume of lead nitrate added and the current recorded from the galvanometer after making volume correction. A reverse L shaped curve will be obtained (Fig.8.13 B type) from which the end point is detected. Calculate the amount of SO_4^{2-} present in the given solution.

1 cm^3 of 0.1 M $Pb(NO_3)_2$ = 0.009606 g SO_4^{2-}

3. Determination of lead with standard dichromate solution.

The potential selected is −1.0 V vs SCE at which both lead ion and dichromate ions give diffusion current. So, the graph obtained will be V shaped (Fig.8.13 C).

Reagents required: 0.001 M $Pb(NO_3)_2$ AR, 0.005 M potassium dichromate and 0.01 M potassium nitrate.

Procedure: To 25.0 cm^3 of 0.001 M $Pb(NO_3)_2$ solution in the cell, add 25 cm^3 of 0.01 M potassium nitrate solution as supporting electrolyte and pass N_2 for 15 minutes. Apply −1.0 V vs SCE and make necessary connections on the polarograph. Add 0.005 M dichromate solution from the microburette in 0.5 cm^3 portion and pass N_2 each time for 1 minute. Note down the readings of the burette and the galvanometer. Initially the current due to Pb^{2+} decreases as dichromate added and increases after the end point with excess dichromate. After making volume corrections draw the graph and note down the end point reading. Repeat this with unknown $Pb(NO_3)_2$ given.

SAQ 11

Give any two advantages of amperometry.

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8.14.3 Titrations with the Rotating Platinum Electrode

Mercury cannot be used as electrode at positive potentials because of its oxidation and therefore rotating platinum electrode at 600 revolutions per minute is used. With platinum as electrode, the attainment of steady state diffusion current is slow and one has to wait for a considerable time after each addition of the reagent and therefore platinum electrode is rotated. The construction of electrode is given below.

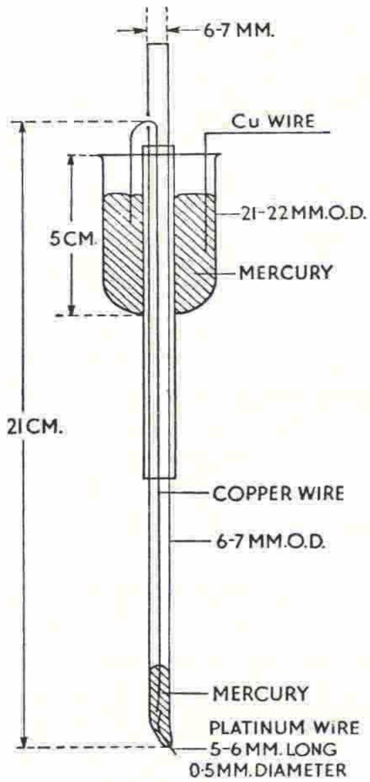

Fig.8.15: Rotating platinum electrode.

i) Determination of antimony (III) with potassium bromate.

Reagents: 0.005 M potassium antimonyl tartrate. 25 cm^3 of this solution is diluted to 250 ml with 1 M hydrochloric acid. Standard 0.002 M potassium bromate solution is prepared in water.

Procedure: Take 25.0 cm^3 of antimony solution into the titration cell and titrate with potassium bromate by setting the applied voltage at +0.2 V vs SCE. Construct the graph as usual and calculate the concentration of antimony solution.

8.14.4 Biamperometry or Dead- Stop End Point Method

In amperometry we use one polarized electrode which may be DME or solid electrode or metallic electrode like platinum and the other reference electrode (non-polarized). In this the potential corresponding to the limiting current plateau is fixed and i_l is measured as function of reagent volume.

In the present method of biamperometry a pair of identical metallic or solid microelectrodes/polarized electrodes are used. The method is very simple and used for the routine and automatic determination of a single species sample. The instrumental setup (Fig. 8.16) is the same as used in amperometry and only SCE is replaced with platinum electrode in the electrolysis cell and a magnetic stirrer is used. A fixed potential difference of 10-20 mV is applied between the two electrodes through the adjustment of resistance variable potentiometer, R (1000 ohms). In such potential difference one electrode will function as an anode and the other cathode. The shape of the titration curves depend on the reversibilities of the oxidation-reduction couples at the electrodes of both sample and titrant used. We get two types of curves for detecting the end point (Fig.8.17 & 8.18).

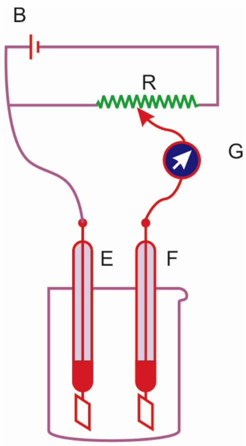

Fig 8.16. Biampero metry instrument

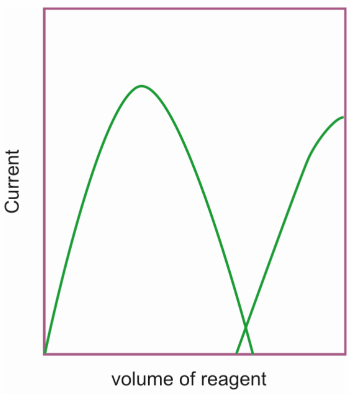

Fig 8.17.

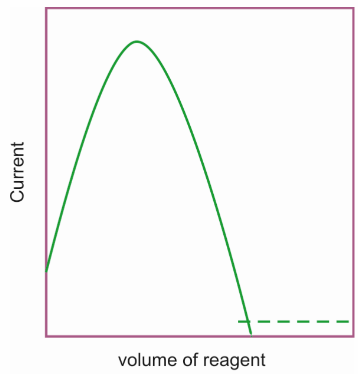

Fig 8.18

i) If both couples (sample and titrant) involved in titration are reversible, we get curve of Fig.8.17. At the end point the current is zero or near zero. Eg: Fe(II) solution in sulphuric acid medium titrated with standard Ce(IV) solution. Fe (II) gets oxidized to Fe(III) as:

$$Fe^{2+} \rightleftharpoons Fe^{3+} + 1\,e^{-}$$

and Ce (IV) reduced to Ce (III) as :

$$Ce^{4+} + 2e \rightleftharpoons Ce^{3+}$$

If the potential difference applied between two electrodes is about 0.2 V no current will flow.

Since the potential difference is very small than the potential difference actually required between Fe(II), Fe(III) couple and Ce(IV), Ce(III) couple, no reaction takes place and no current will flow before the titration started. Only when the potential difference between two electrodes is about 0.7 V, the oxidized form Fe(III) at anode will reduce back to Fe(II) at the cathode. But in titrations when Ce(IV) solution is added from the burette, equivalent amount of Fe(II) from the electrolytic cell will be producing Fe(III) and can be reduced at the cathode. In this, Fe(III) is produced not by electrode reaction of oxidation of Fe(II) but by the reaction with Ce(IV) which can be reduced to Fe(II) at the cathode. Since the couple Fe(II) and Fe(III) are present in solution, Fe(III) is reduced at cathode and Fe(II) is oxidized at anode. This is because the Fe(III)– Fe(II) couple is reversible and even little potential difference between two electrodes is enough when both are in the solution. As more and more Ce(IV) solution is added from the burette more and more Fe(III) being produced and Fe(II) concentration in the solution is reduced. So, with more Fe(III) ion being produced, the current will be rising in proportion until the concentration of Fe(III) ion equals that of Fe(II) ion. If the titration is continued further, the current will decrease since the amount of Fe(II) ion available for reaction at the anode becomes smaller. Finally, when all Fe(II) is removed by titration with Ce(IV), at the equivalence point, the current will be almost zero because no Fe(II) ion is present in the solution to oxidize at the anode. At this stage, cathode will reduce Ce(IV) ion rather than Fe(III) ion. This is because its couple Fe(II) is not existing in solution and anode will be able to oxidize Ce(III) ion. With more and more Ce(IV) ion added, current further increases. So during the titration, the current will rise from nearly zero to a maximum at the mid point of the titration, decrease to zero at the equivalence point, and finally rise again to give a graph of Fig. 8.17.

Other examples : Titration of azobenzene in acidic solution with V(II)

ii) If one of the couples is irreversible the shape of the curve will be different.

Eg: titration of iodine by thiosulphate. In this, iodide-iodine couple is reversible and titrant thiosulphate-tetrathionate couple is irreversible. The titration curve will be as in Fig 8.18.

$$I_2 + 2e^- \rightleftharpoons 2I^-$$

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^-$$

When iodine in a solution containing iodide is titrated with thiosulphate, the anode will oxidize iodide ion and cathode will reduce iodine because iodide-iodine couple is reversible. As more and more iodine is removed from the solution by adding more and more thiosulphate the current will decrease, since there is less iodine available for reduction at the cathode. Finally, at the end point, the iodine is completely removed from the solution and the current will be nearly zero. After the end point, as more thiosulphate is added, the current remains the same because the titrant couple is irreversible and the applied potential value is small.

Other examples: Titration of azobenzene in dilute hydrochloric acid with chromium ion.

SAQ 12

a) What type of electrodes are used in biamperometry?

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b) What should be the potential difference between two electrodes in biamperometry, so that the Fe (III) will be reduced back to Fe (II)?

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c) What will be the shape of the curve in bioamperometry for the titration of iodine by thiosulphate?

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8.15 SUMMARY

In this unit, we have discussed about the theory of Polarography and Amperometric titrations. We started our discussion with a typical polarogram and then the dropping mercury electrode (DME). After that we discussed in detail the advantages of a DME and continued our discussions on limiting and migration current, followed by diffusion and residual current. The factors affecting residual current were then discussed. Half wave potential, $E_{1/2}$, and effect on complexing agents on it were dealt with. The determination of n and reversibility were discussed taking the log plot of Cd(II) in 1 M KCl. Discussion of kinetic currents, catalytic currents, adsorption waves, polarographic maxima and maximum suppressors were then done. Discussion on qualitative as well as quantitative polarographic analysis including calibration plot, internal standard method and method of standard addition were done. We concluded our discussion on Polarography with the instrument involved in polarographic analysis. This was followed with detailed discussion about the amperometric titrations where we started with the advantages of amperometry followed by a few examples of amperometric titration.

8.16 TERMINAL QUESTIONS

1. Give three reasons for using a dropping mercury electrode in polarography.

2. Define half-wave potential, diffusion current, kinetic current, catalytic current and residual current.

3. Why is a high supporting electrolyte concentration used in most electroanalytical procedures?

4. What is the effect of complexing agent on the reduction of metal ion in Polarography?

5. Derive polarographic equation.

6. Write Ilkovic equation and define the terms.

7. A mixture containing Tl^{+}, Cd^{2+}, and Zn^{2+} exhibited the following diffusion current in two different experiments A and B, run with same electrolyte on different occasions:

		Concentration (mM)	**I_d (μA)**
Tl^{+}:	A	1.15	6.38
	B	1.21	6.11
Cd^{2+}	A	1.02	6.48
	B	?	4.76
Zn^{2+}	A	1.23	6.93
	B	?	8.54

Calculate the Cd^{2+} and Zn^{2+} concentrations in experiment B.

8. A metal ion M is reduced in a supporting electrolyte with a two electron change and the half wave potential is reported at − 0.405V vs SCE. When a ligand L is added in different concentrations, the following shift has been observed. Find out stoichiometry of the complex and the value of its formation constant.

Conc. of ligand added (M)	half wave potential of the complex (V)
0.02	−0.473
0.06	−0.507
0.10	−0.516
0.30	−05.47
0.50	−0.558

9. On what factors does the migration current depend on? Explain with the help of an equation.

10. For what have the adsorption waves been used?

11. Explain the method of standard addition in quantitative polarographic analysis?

12. Explain the procedure of determination of Zn with EDTA with the help of amperometry.

13. Is amperometric titration capable of greater accuracy than non-titrative polarographic method?

14. Explain different types of titration curves obtained in amperometry giving examples.

15. A rotating platinum electrode is preferable over DME in which situation?

16. Give the titration curve expected when Fe(II) is titrated with Ce(IV) solution in acid medium using two platinum electrodes.

17. Define the components of a simple polarography.

18. If several different complexing agents are present in the solution, how will this affect the polarographic behaviour?

8.17 ANSWERS

Self-Assessment Qestions

1. The polarographic method of analysis was developed by Jaroslav Heyrovsky in 1922 which is the earliest voltammetric technique introduced. This technique uses dropping mercury electrode as the working electrode. The recorded current-potential curves are known as polarograms.

2. a)The dropping mercury electrode has the following advantages:

   i) Its surface area is reproducible with a given capillary

   ii) The constant renewal of the electrode surface eliminates passivity or poisoning effects.

   iii) The large hydrogen overpotential on mercury renders possible the deposition of substances difficult to reduce such as aluminium ion and manganese (II) ion (The current-potential curves of these ions are not accessible with platinum micro electrode).

   iv) Mercury forms amalgams with many metals.

   v) The diffusion current assumes a steady value immediately and is reproducible.

   vi) The surface area of the electrode can be calculated from the weight of the drops.

   b) Current–voltage curves obtained with electro-reducible ions at DME are frequently distorted by increasing the current beyond the diffusion current value and rapidly decrease to the normal diffusion plateau after a critical value is reached as the applied potential is increased. This abnormal increase in current is referred as maxima and vary in shape from sharp peaks to rounded humps.

c) Potential range of DME is + 0.3 to −2.0 Volts vs SCE.

3. a) The migration current is due to the migration of reducible or oxidizable ions which is proportional to the electrical potential gradient at the electrode due to attraction.

   b) This migration current is usually eliminated by adding 50 or 100 fold excess of an inert supporting electrolyte.

4. a) In the absence of electroactive substance in the solution having only supporting electrolytes, a small current is always present which is referred as residual current.

   b) Limiting current is regarded as the sum of 'diffusion current' and a 'migration current'. Whereas, in the presence of excess supporting electrolyte the electrical force on the reducible/oxidizable ions is nullified and therefore, the limiting current is solely a diffusion current.

5. a) It is seen that the diffusion current depends on m and t (together referred as capillary characteristics) and are therefore affected by their variations. 'm' is directly proportional and 't' is inversely proportional to the net pressure on the mercury drop.

   b) Refer to Section 8.6.3

6. Refer to Eq. (8.13) of Section 8.7. It represents the potential as a function of current at any point on the polarographic wave.

7. The reversibility of electrode reaction can be determined simply and rapidly by measuring the potential corresponding to ¼ and ¾ from the polarogram. By this method we get for a reversible cathodic wave the value of $E_{3/4} - E_{1/4}$ to be equal to $-\frac{56.4}{n}$ mV and for reversible anodic wave it is equivalent to $+\frac{56.4}{n}$ mV.

8. Some electroactive species or their products due to electrooxidation or reduction are adsorbed on the surface of mercury drop and give adsorption waves.

9. To measure the true diffusion currents the maximum must be eliminated. This can be done by adding small amount of surface-active agents such as gelatin, dye stuff, Triton X-100 etc. which are likely to form an adsorbed layer on the mercury–solution interface to prevent streaming movement of the diffusion layer at the interface.

10. Fig. 8.11.

11. Refer to Section 8.14.1 and give any two advantages.

12. a) In the present method of Biamperometry a pair of identical metallic or solid microelectrodes/polarized electrodes are used.

    b) Only when the potential difference between two electrodes is about 0.7 V the oxidized form Fe(III) at anode will reduce back to Fe(II) at the cathode

    c) Fig 8.17

Terminal Questions

1. The reasons for using dropping mercury electrode are:

   i) Mercury forms amalgams with many metals.
   ii) The diffusion current assumes a steady value immediately and is reproducible.
   iii) The surface area of the electrode can be calculated from the weight of the drops.

2. Half wave-potential, $E = E_{1/2} = E^0 - \frac{0.059}{n} \log \frac{K_1}{K_2}$

   Diffusion current : The presence of excess supporting electrolyte the electrical force on the reducible/oxidizable ions is nullified and therefore, the limiting current is solely a diffusion current. (For details refer to Eqn 8.3)

   Kinetic currents: Refer to Section 8.10.1 and Eq. (8.19).

   Catalytic currents: Refer to Section 8.10.2 and Eq. (8.21), (8.22) and (8.23).

   Residual Current: Refer to Section 8.5.2.

3. According to Ilkovic equation, i_d is proportional to $\eta^{1/2}$. η varies as the aqueous solution changed partly to non-aqueous medium using solvents such as methanol, dioxane etc. Changes in the composition of the supporting electrolyte by adding complexing ligands to the electrolyte solution changes the size of the metal complex and therefore D of the ion. i_d therefore decreases with complexation and $E_{1/2}$ shifts to more negative potentials.
   It is necessary to keep the concentration of every constituent of the supporting electrolyte constant within about $\pm$ 10% to ensure the variation of i_d resulting from this effect (viscosity) will be negligibly small.

4. In case of complexation of metal ion with the complexing agent, $E_{1/2}$ of the metal ion is shifted to more negative value compared to the reduction of simple metal ion in the non-complexing medium. For details refer to Eq (8.16) and (8.17).

5. Refer to Eq. (8.5) to (8.13).

6. $i_d = 607\, n\, c D^{1/2} m^{2/3} t^{1/6}$
   Refer to the details in Eq (8.3) of section 8.5.1.

7. Cd^{2+}=0.81; Zn^{2+}=1.66M

8. M:L=1:2; $K_f = 7.2 \times 10^5$

9. The migration current depends on the transference number of the reducible or oxidizable ion in the solution and the total limiting current. Refer to Eq. (8.2)

10. The adsorption waves have been used to evaluate the area of adsorbed species using the equation given below when only adsorption is seen without normal wave.

    $i_a = 13.66\, n\, m^{2/3} t^{-1/3} / A$

    where 'A' is the area (in Å) covered by each adsorbed molecule.

11. Refer to section 8.12 and Eq. (8.26).

12. Determination of Zinc with EDTA (details in 1st paragraph of section 8.14.2).

13. A number of amperometric titrations can be carried out at dilutions (ca 10^{-4} M) at which many visual or potentiometric titrations no longer yield accurate results. The results of the titration are independent of the characteristics of the capillary. So amperometric titration is capable of greater accuracy than non-titrative polarographic method.

14. The voltage applied at the beginning of the titration must be selected so that the diffusion current of the substance to be titrated or of the reagent or of the both, is obtained. Depending on the selection of the applied voltage between DME and reference electrode various types of titration curves are obtained (details in Fig. 8.13)

15. Mercury can not be used as electrode at positive potentials because of its oxidation and therefore rotating platinum electrode at 600 revolutions per minute is used. With platinum as electrode the attainment of steady state diffusion current is slow and one has to wait considerable time after each addition of the reagent and therefore Pt electrode is rotated.

16. When both couples (sample and titrant) involved in titration are reversible, we get curve of Fig. 8.16. At the end point the current is zero or near zero. Refer to section 8.14.4, 2nd and 3rd paragraph.

17. Figure 8.14 (b)

18. Refer to section 8.8.2, Fig. 8.5, Eq (8.16) and (8.17).