EXPT .9 IDENTIFICATION AND DETERMINATION OF $Cd^{2+}/Pb^{2+}/Zn^{2+}$ POLAROGRAPHICALLY

Structure

9.1 INTRODUCTION

A detail of polarographic methods is already disused the Units 8 and 9 of MCH -004 course. In this experiment you are going to identify and determine Cd^{2+}, Pb^{2+}, and Zn^{2+} using polarographic method. You will use a polarogram for the identification of cations and use calibration technique for estimations of the concentrations of cations in given solutions.

Objectives

After performing this experiment you will be able to:

- Record polarograms of Cd^{2+}, Pb^{2+}, and Zn^{2+} ions,
- determine the concentrations of Cd^{2+}, Pb^{2+}, and Zn^{2+} ions in the given solutions using polarograph,
- determine the concentration of Cd^{2+}, Pb^{2+}, and Zn^{2+} ions from their calibration graph,
- state the advantages polarographic methods in qualitative and quantitative analysis, and
- practice the precautions while performing polarographic experiment.

9.2 PRINCIPLE

Polarography can be used for the determination of trace amount of many different metal ions. It is an electrolysis technique in which microelectrolysis is carried out at a dropping mercury electrode (DME) in an unstirred solution. The data are obtained as a current voltage curve that is characteristic of the electro-active materials. A typical instrument called polarograph and cell is shown in Fig. 9.1

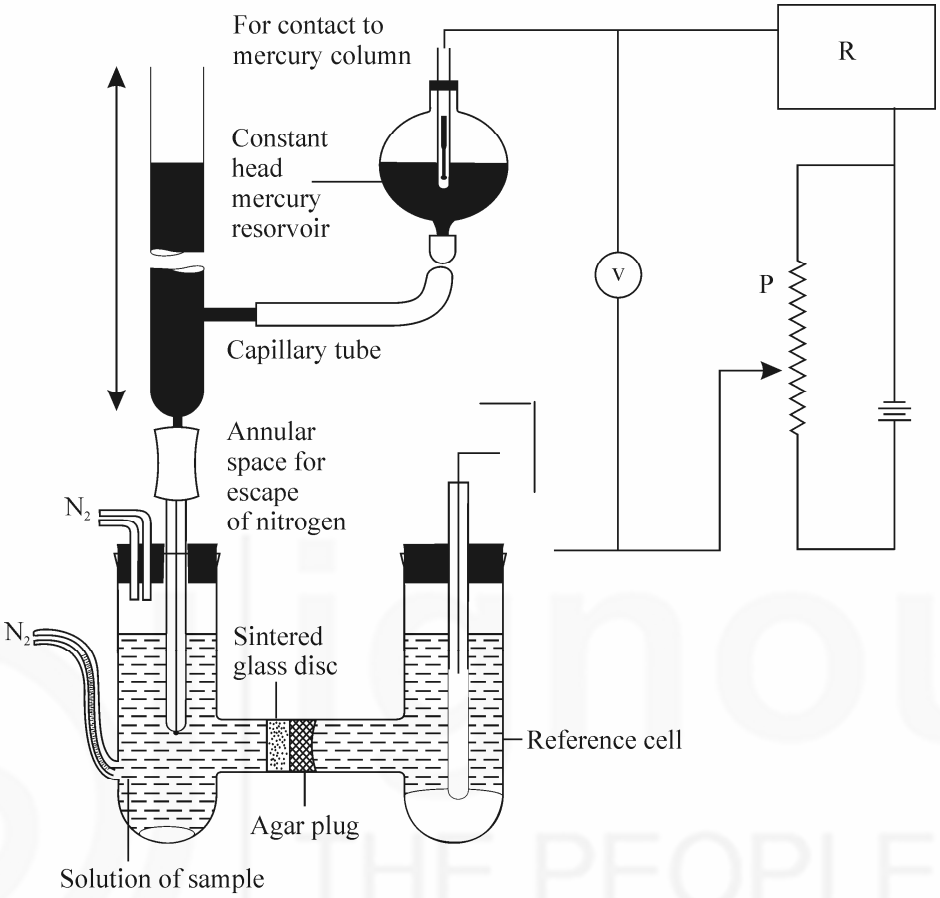

Fig. 9.1: The polarograph and cell

The potential on the dropping mercury electrode can be varied by changing the contact point on the slide wire. At each applied potential the current is measured with ammeter. A typical cell consists of a reference electrode (calomel electrode) and a working electrode (DME) separated by a sintered glass disc or other porous media. If test solution is placed in the cell and the voltage of the DME is continuously made more negative (with respect to the reference electrode), a curve called a polarogram will be obtained. A typical polarogram is shown in fig. 9.2.

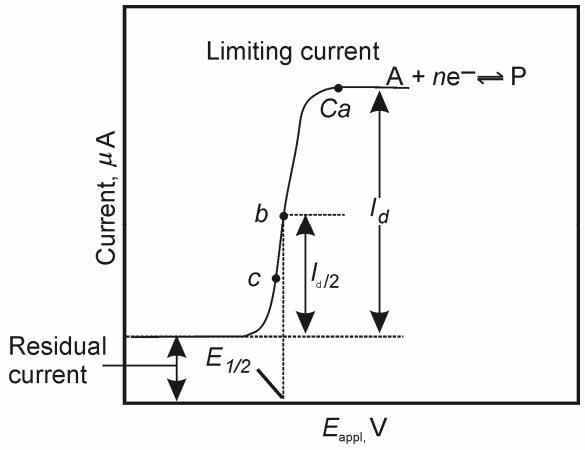

Fig. 9.2: A typical polarogram

Several different kinds of currents contribute to the polarogram. They are residual current, diffusion current and the supporting electrolyte current. The migration current can be minimized by adding supporting electrolyte in large concentration relative to the electro-active material. In the presence of excess of supporting electrolyte the diffusion current can be related to the concentration, c, through the Ilkovic equation:

$$i_d = 708\ ncD^{1/2}\ m^{2/3}\ t^{1/6} \qquad \ldots(9.1)$$

where i_d is the diffusion current as an average in micro amp, n is the number of electron in the reaction per mol, c is the concentration in mmol/dm^3, D is the diffusion coefficient in cm^2/sec, m is the rate of flow of Hg in mg/sec, and t is the drop time in seconds. It the mass and drop time are held constant, Eq. 9.1 can be reduced to

$$i_d = k'c$$

where K' include the parameters which are held constant. In most applications, the polorogram is run with the solution under nitrogen atmosphere since oxygen is polarographacally active.

Half-wave potentials are also characteristic of a particular electro-active material and it can be used for qualitative applications. Half wave potential corresponds to the point of inflexion of the pologrphic curve (see Fig.9.2)

Two general techniques are utilized in quantitative polorography. Since i_d is proportional to concentration a calibration curve can be prepared by measuring i_d for a series of standards of known concentrations at a potential on the limiting current part of the curve (Fig. 9.3).

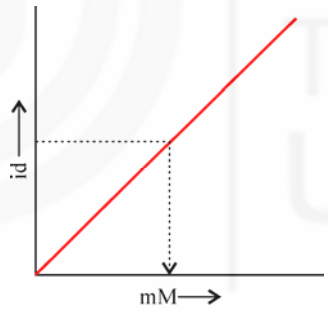

Fig. 9.3: Calibration plot

The second method is based on the internal standard principle. A known concentration of an electro-active reference ion is added to the unknown solution and i_d's for the two reported polorogram are measured. The concentration of the unknown is calculated from

$$c_{unk} = c_{std}\ \frac{i_{d\,unk}}{i_{d\,std}}$$

9.3 REQUIREMENTS

Apparatus

Polarograph with polarographic cell, SCE, DME, volumetric flask, pipette, graduated flask, beakers, arrangement for passing nitrogen gas.

Chemicals

Potassium chloride, potassium nitrate, cadmium sulphate, zinc sulphate, lead sulphate and gelatin.

9.4 PROCEDURE

A. Identification of Cd^{2+}, Pb^{2+} and Zn^{2+}

1. Pipette 10 cm^3 cadmium sulphate solution (1.0 g $CdSO_4$ in 1 dm^3 distilled water) in a 100 cm^3 graduated flask, add 2.5 cm^3 of 0.2 percent gelatin solution, 50 cm^3 of 2 M KCl solution and diluted to the mark. This solution contains 0.10g/dm^3 Cd^{2+} ions and 1.0 M KCl (supporting electrolyte)

2. Place 5.0 cm^3 of above solution in a polarographic cell equipped with an external reference electrode (SCE). Pass pure nitrogen through the solution at a rate of about two bubbles per second for 10-15 minutes in order to remove dissolved oxygen. The height of the mercury column is adjusted so that the flow rate is approximately 1 drop per 5 second.

3. Connect the SCE to positive terminal and DME to the negative terminal of the polarograph. Stop the passage of nitrogen gas through the solution.

4. Record the polarogram in steps of 0.05 V from – 0.0 V to – 2.0 V vs. SCE or you may follow instructions given in the manual of the polarograph or the direction given by the instructor. This will result a polarogram similar to Fig. 9.2

5. Determine half-wave potential which is – 0.676 ± 0.004 volts vs. SCE.

   Similarly we can identify Zn^{2+} and Pb^{2+} using KCl and KNO_3 supporting electrolytes for Zn^{2+} and Pb^{2+}, respectively. Normally their $E_{1/2}$ value and – 1.2 V and – 0.40 V respectively in these supporting electrolyte however their value may differ slightly depending upon the concentration of the supporting electrolyte.

B. Determination of Cd^{2+}, Pb^{2+} and Zn^{2+} by calibration method:

1. Prepare from the stock solution containing 1.000 g of Cd^{2+} per dm^3. From the stock solution prepare respectively 0.1, 0.05, 0.025, and 0.01 g Cd^{2+} per dm^3 by transferring 10, 5.0, 2.5 and 1.0 cm^3 to a 100 cm^3 graduated flasks, than add 50 cm^3 of 2 M KCl solution and 2.5 cm^3 of 0.2% gelatin solutions to each flask and finally dilute to the mark with distilled water and mix them toughly.

2. Take 10 cm^3 of the unknown sample (that may contain 0.04 g of Cd^{2+}/dm^3) in a 100 cm^3 graduated flask and add to it 50 cm^3 of 2 M KCl and 2.5 cm^3 of 0.2% gelatin solutions and dilute to the mark with distilled water.

3. Record the polarograms of the four standards solutions and the unknown solution following the procedure discussed for Procedure A. Determine the wave heights from each of the polarograms. Draw a calibration curve (wave heights on y axis and concentration on x axis) for the four standard solutions.

4. Find out the concentration of unknown solution from the drawn calibration curve.

Following similar procedure we can determine Zn^{2+} and Pb^{2+} in their unknown solutions.

Precaution

1. The concentration of the supporting electrolyte should be kept constant through out the experiment, since the $E_{½}$ and i_d depend on it. The other parameters specially, the drop time and temperature are also equally important.

2. The concentration of maximum suppressors (gelatin) should be at as low as possible since it affects the value of the diffusion current.

3. After completion of the experiment. The capillary must be with-drown from the cell, wash thoroughly. The electrode the capillary may be blocked. The used mercury should be covered with water since, its vapours are toxic.

4. DME and SCE should be correctly immersed in the test solution, other wise electrolysis will not complete.