EXPT. 10 AMPEROMETRIC DETERMINTION OF LEAD (II) WITH POTASIUM DICHRORIATE

Structure

10.1 INTRODUCTION

A detail of amperometric titrations is already disused the Units 8 and 9 of MCH -004 course. In this experiment you are going determine lead by amperometric titration method with potassium dichromate. You will use amperometric titration curve for identification of the end point.

Objectives

After performing this experiment you will be able to:

- Draw amperometric titration curve for the titration of lead ions with potassium dichromate solution,
- determine the concentrations of lead ions in the given solutions using polarograph,
- state the advantages of amperometric titrations, and
- practice the precautions while performing amperometric titration experiment.

10.2 PRINCIPLE

As discussed in Unit 8, in polarography, it is well established that if the residual and migration current are eliminated i.e. residual current by blank correction / or extrapolation method and migration current by using a suitable supporting electrolyte, then the diffusion current, i_d = limiting current – residual current, after suppression of migration current with the use of a supporting electrolyte is proportional to the concentration of the electro-active material in a solution or ($i_d \propto c$). If some of the electro-active material is removed by interaction with a reagent, the diffusion current will decrease according. This is the bank principle of amperometric titrations. The observed diffusion current/ at a suitable applied potential is measured as a function of the standard volume of the titrating solution, the end point is the point of intersection of two lines giving change of current before and after the equivalent point.

In the present case, lead (II) and $Cr_2O_7^{2-}$ /CrO_4^{2-} give well defined polarograms and both of these ions yield a diffusion current at an applied potential to a dropping mercury electrode (MME) at –1.0 V against the saturated calomel electrode (SCE) in the presence of 0.01M KNO_3 solution as the supporting electrolyte. With the addition of $K_2Cr_2O_7$, the diffusion current of lead starts decreasing and after the end point, the diffusion current due to $Cr_2O_7^{2-}$ ions starts increasing. Thus a 'V'- shaped curve will be obtained (Fig. 10.1).

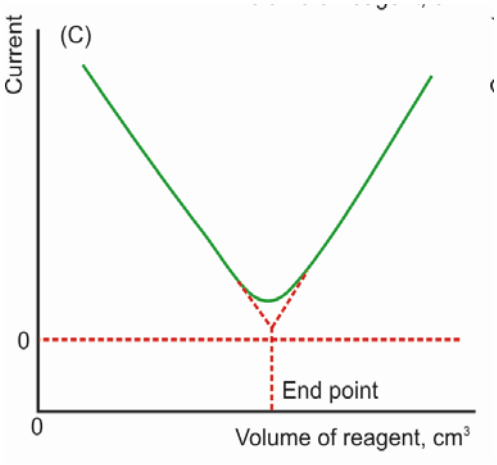

Fig. 10.1: A typical amperometric titration curve

Lead (II) is an unknown solution can be determined. The ratio is which Pb^{2+} reacts with $Cr_2O_7^{2-}$ can be worked out from the value of the diffusion current at the equivalent point, it is possible to calculate the solubility product of $PbCrO_4$ provided diffusion current constants of Pb^{2+} and $Cr_2O_7^{2-}$ under these conditions are calculated from their respective polargrams. [$(I_{Pb^{2+}} = i_d$ (at equivalent point)$/c_{Pb^{2+}} m^{2/3}t^{1/6}$, similarly, $(I_{CrO_4^{2-}} = i_d$ (at equivalent point)$/c_{CrO_4^{2-}} m^{2/3}t^{1/6})$].

A reverse titration of $Cr_2O_7^{2-}$ solution in the polarographich cell and titrated Pb^{2+} solution in the burette as titrant can also be carried out.

10.3 REQUIREMENTS

Apparatus

A polarograph, a 100 cm^3 Pyrex glass beaker with a suitable cover may used, a semi micro type and graduated pipettes of 0.01 cm^3 may be used for titration, a dropping mercury electrode with a proper drop time (3-4 drops/sec) is used in the present case. A saturated calomel electrode, a agar-salt bridge is made of a gel that is 3% agar with sufficient KNO_3 (20-25g) in 100 cm^3 solution at room temperature (KCl is normally used in the agar-salt bridge, since it will interfere with Pb^{2+} so it is replaced with KNO_3 in the present case). The complete set-up in shown in Fig.10.2

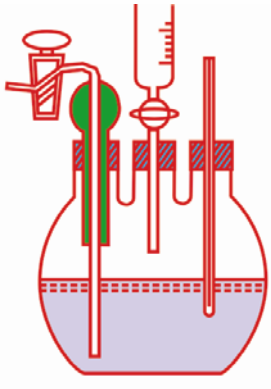

Fig. 10.2: A typical titration cell used in amperometric titrations

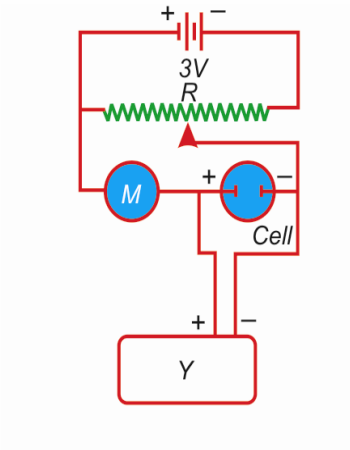

Fig. 10.3: A simple electrical circuit diagram suitable for an amperometric titration

Reagents

Lead nitrate solution: Dissolve an accurately weighed amount of lead nitrate in 250-cm^3 water is a graduated flask to give approximately 0.01M solution. For the titration, purpose take 10 cm^3 this solution with the help of pipette to 100 cm^3 in a graduated flask and dilute it with water, the find solution will be 0.001 M $Pb(NO_3)_2$.

Potassium dichromate: prepare 0.005 M solution is distilled water with appropriate amount of $K_2Cr_2O_7$ sample. In case $K_2Cr_2O_7$ is no available K_2CrO_4 may be used as a titrant.

Potassium nitrate (0.01 M) as a supporting electrolyte.

10.4 PROCEDURE

1. Use any commercial or a manual polarograph and follow the instruction given in the manual of the instrument or by the counsellor. Set the DME and allow the mercury to drop into distilled water for 5 minutes. Now pipette 25.0 cm^3 of 0.001 M lead nitrate solution in the titration cell (Fig.3), add to it 25.0 cm^3 of 0.0 1 M KNO_3 solution, complete the cell assembly, and pass nitrogen gas through the solution for 5nminutes.
2. Make the necessary electrical connection. Apply a potential of –1.0 vs. SCE, at this applied potential both lead and dichromate ions yield diffusion current. Adjust the galvanometer sensitivity to almost full scale and note the reading. Do not alter the applied potential during the determination.
3. Add 0.005 M $K_2Cr_2O_7$ solution in 0.5 cm^3 increments until 1 cm^3 of the end point and henceforth in 0.1 cm^3 till about 1 cm^3 beyond the end point and continue with the addition of 0.5 cm^3. After each addition pass nitrogen through the solution for 1 minute, to ensure through mixing and de-oxygenation, stop the flow of nitrogen and note the deflection of the galvanometer, i.e. measure the current.

It will be observed that a large initial current will decrease as the titration proceed to a small value at the equivalence point and then increases again beyond the equivalence point. Correct the reading of the galvanometer deflection for the change is volume of the solution due to added reagent using the relationship $^{c}\text{orrected} = i_{obs.} \times (V+v)/V$. where V in the initial volume of the solution and v is the volume of the titrating reagent. Plot the volume of the corrected current (galvanometer defection) as ordinate against the volume of the reagent added as abscissa; draw to straight lines through the branches

of the curve similar to Fig 10.1. The point of interaction is the equivalence point. Calculate % of lead in the sample of lead nitrate.

Experiment may also be carried out with a semi micro burette of 5-10 cm^3 using 0.05 M $K_2Cr_2O_7$ solution.

10.5 CALCULATIONS

Apply the equimolar relationship,

1 cm^3 of 0.00 1 M $K_2Cr_2O_7$ = 0.002072 g of Pb

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.

10.6 RESULTS

Precautions

1. Temperature of solution and the concentration of supporting electrolyte must be kept constant during the titration.
2. DME and SCE should properly clip is the sample solution to have a complete circuit.
3. The titrant must be at least 10 times stronger then the analyte, otherwise one has to apply the dilution correction. The correction can be accomplished by multiplying the observed current by a factor $(V+v)/V$, where V is the volume of solution and v is the volume of the reagent added from the burette.
4. If the pH of the solution is < 6.5, CrO_4^{2-} may not be completely generated from $Cr_2O_7^{2-}$, in such case a few cm^3 of 0.01 M sodium acetate salt may be added

before the titration or titration may be carried out with K_2CrO_4 solution instead of $K_2Cr_2O_7$.

$$Cr_2O_7^{2-} + H_2O = 2\,CrO_4^{2-} + 2\,H^+$$

So pH should be in the range of 6.5-9.0.

5. The applied potential should kept constant during the titration
6. Work out the stereochemistry in includes Pb^{2+} and $Cr_2O_7^{2-}$ reacts. A reverse titration may be performed with $Cr_2O_7^{2-}$ in the cell and Pb^{2+} in the burette and predict the shape of the titration curve.
7. Extlain why do we advise not to measure the current in the vicinity of the end-point in emperometry and coulometric titration.