EXPERIMENT 15
ESTIMATION OF MAGNESIUM AND CALCIUM IONS IN A MIXTURE BY COMPLEXOMETRY

Structure

15.1 INTRODUCTION

In Chemistry Lab-I and Chemistry Lab-II courses, you performed titrimetric or gravimetric estimations of only single cation present in any substance. In this experiment and Experiments 15 and 16, you will perform titrimetric or gravimetric estimations of two cations together. For example, you will determine i) magnesium and calcium by complexometry; ii) copper and zinc, and iii) copper and nickel by gravimetry. Now we will concentrate on complexometric titration method.

Numerous methods are available for titrimetric determination of various cations by titrations of their salts with certain organic reagents called complexones. These complexones are imino-polycarboxylic acids, having excellent complex forming ability with a number of cations. The simplest of the complexones is iminodiacetic acid, $HN(CH_2COOH)_2$. Other complexones can be assumed to be higher derivatives of this family. The most important member of this family of reagents is ethylenediaminetetraacetic acid, abbreviated as EDTA. The structure of EDTA is shown in Fig. 15.1.

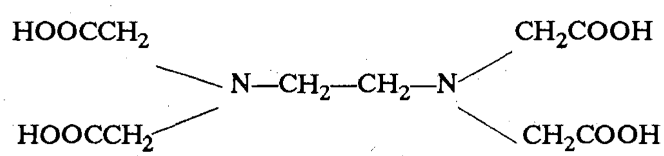

Fig. 15.1: The structure of EDTA

EDTA can form complexes with a number of cations like alkaline earth metals and many non-ferrous metal ions like Cu^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Mn^{2+}, Bi^{3+}, Zr^{4+} and Hf^{4+}, etc.

EDTA is only slightly soluble in water. However, its disodium salt is freely soluble in water. Dihydrate of the disodium salt is available commercially in a state of high purity under the brand names 'Versen' or 'Trilon-B'. It can be used as a primary standard. EDTA, generally, forms 1:1 complexes with metal ions. In reactions, EDTA and its disodium salt are represented as H_4Y and Na_2H_2Y, respectively. Reaction of the disodium salt with a bivadent cation can be written as follows:

$$Na_2H_2Y \longrightarrow 2Na^+ + H_2Y^{2-}$$

$$H_2Y^{2-} + M^{2+} \longrightarrow MY^{2-} + 2H^+$$

It is apparent from the above equation that there is always a competition in solution between the metal ions and the hydrogen ions in seeking the negative sites on EDTA. The equilibrium condition is determined by the strength of the bond between the metal ion and the ligand, and the relative concentrations of metal ions versus hydrogen ions. In other words, we can say that the stability of the metal-EDTA complex will be governed by the hydrogen ion concentration or pH of the solution. Minimum pH values for the stability of EDTA complexes of some selected metal ions are listed in Table 15.1

Table 15.1: Stability with respect to pH of some Metal EDTA complexes

Sl.No.	Metal ion	Minimum pH at which complex is stable
1.	Bi^{3+}, Zr^{4+}, Hf^{4+}, Th^{4+}	1 - 3
2.	Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Sb^{2+}, Fe^{2+}	4 - 6
3.	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	8 - 10

You can see from the Table that in general, EDTA complexes with alkaline earth metal ions are stable in alkaline solution, whilst complexes with tri- and tetra-valent metal ions are stable in strongly acidic solutions.

EDTA is a multidentate ligand as it can donate six paris of electrons - two pairs from the two nitrogen atoms and four pairs from the four terminal oxygens of the $-COO^-$ groups. Such multidentate ligands prefer to form complexes having ring type structures. As you know, these complexes are called chelates and such ring forming ligands are called chelating agents.

The structure of a chelate of a divalent metal ion with EDTA is shown in Fig. 15.2.

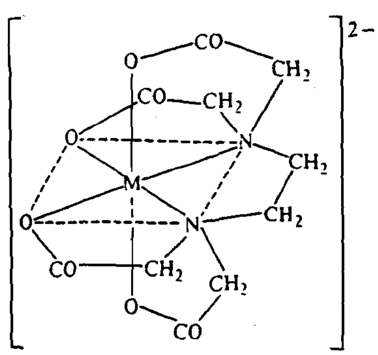

Fig. 15.2: The structure of a chelate of M^{2+} and EDTA

Objectives

After studying and performing this experiment, you should be able to:

- estimate Ca^{2+} and Mg^{2+} together by complexometry, and
- describe complexones and perform complexometric titration

15.2 PRINCIPLE

In complexometric determination of magnesium and calcium ions in their mixture, EDTA is used as a titrant and Solochrome Black (Eriochrome Black T) as an indicator. When indicator solution, which is blue in colour, is added to the solution containing magnesium and calcium ions, wine red coloured metal ion-indicator complexes of varying stability are formed. The magnesium-indicator complex is more stable than the calcium indicator complex but less stable than the magnesium-EDTA complex which in turn is less stable than the clacium-EDTA complex. Consequently, when EDTA solution is added, it reacts first with the free calcium ions, then with the free magnesium ions, then with the calcium indicator complex and finally with the magnesium-indicator complex. Since the magnesium-indicator complex is wine-red in colour and the free indicator is blue between pH 7 and 11, the colour of the solution changes from wine-red to blue at the end point.

In this experiment, we titrate one portion of the test solution containing both magnesium and calcium ions with EDTA using Solochrome Black indicator at pH 10 and the volume consumed is noted. This gives the volume of EDTA required for the titration of both magnesium and calcium ions. Then another equal portion of test solution is taken, but this time the medium is kept strongly alkaline. In strong alkaline medium, magnesium ions are precipitated and the calcium ions are left free in the solution. This solution is then titrated with EDTA for calcium ions only using Murexide as indicator. The volume of EDTA consumed is the volume required for titration of calcium ions only. By substracting the volume of EDTA consumed by calcium ions from the volume of EDTA required for both magnesium and calcium ions, we get the volume required for magnesium ions.

As EDTA is a primary standard, its molarity is known. Then using the molarity equation, $M_1V_1 = M_2V_2$, the molarity of magnesium and calcium ions can be calculated.

15.3 REQUIREMENTS

You will need the following apparatus, chemicals and solutions for this experiment.

Apparatus		**Chemicals**
Beaker 250 cm^3	1 No.	Ammonia liquor
Burette 50 cm^3	1 No.	Ammonium chloride
Burette stand	1 No.	Calcium chloride
Conical flask 250 cm^3	1 No.	Disodium salt of EDTA
Funnel	1 No.	Magnesium sulphate
Pipette 20/25 cm^3	1 No.	Murexide indicator
Pipette graduated 10 cm^3	1 No.	Sodium hydroxide
Volumetric flask 250 cm^3	1 No.	Solochrome Black indicator
Wash bottle	1 No.	
Weighing bottle	1 No.	

Solutions provided :

1. **Test solution :** It can be prepared by dissolving accurately 2–3 g of calcium chloride and 1–2 g of $MgSO_4$ into minimum quantity of dil. HCl and making up the volume to 250 cm^3 with distilled water.

2. **$NH_3 - NH_4Cl$ buffer solution of pH 10 :** This can be prepared by dissolving 64g of NH_4Cl in distilled water, adding 570 cm^3 of ammonia solution (sp.gr. 0.88) and diluting to 1dm^3 with disttled water.

3. **Solochrone Black indicator (0.5% mass /volume) :** 0.50 g indicator is weighted and dissolved in 100 cm^3 ethanol.

4. **Mureride indicator :** It can be used as solid, in 0.05g quantity in each titration. The indicator solution may be prepared by suspending 0.5g of the powered solid in

water, shaking thoroghly, and allowing undissolved protion to settle. The saturated supernant liquid is used for titrations. Every day the old supernatant liquid decanted and the residue treated with water as before to provide a fresh solution of indicator. 3–4 drops of this solution are used for each litration.

5. **0.1 *M* NaOH solution :** Dissolve 4 g of NaOH in 1 dm^3 of distilled water.

15.4 PROCEDURE

The experimental procedure involves the following steps:

1) **Preparation of standard 0.1*M* EDTA solution:** As said earlier, EDTA is available as a dihydrate of its disodium salt ($Na_2H_2Y.2H_2O$). Take already dried disodium salt of EDTA from your counsellor. Take rough mass of a glass weighing bottle, transfer about 9.5 g of the salt to the weighing bottle and weigh accurately. Transfer the salt to a clean and dry volumetric flask of 250 cm^3 capacity through a glass funnel. Find out the accurate mass of the weighing bottle after transferring the salt. The difference between the two masses gives the actual mass of the salt taken. Record these values in your observation note book for calculating the exact concentration of the solution. Now dissolve the salt in deionised or distilled water. Make up to the mark with distilled water and shake thoroughly to make a homogeneous solution.

2) **Titration of the test solution**

In this titration colour change develops a little late, hence, titration should be done slowly. If necessary, add 2-3 drops more of indicator at the final stage of titration. This will provide necessary contrast in colour.

i) Fix a clean burette in a burette stand.

ii) Fill the burette with the EDTA salt solution after rinsing it with this solution and mount the burette on a stand. Note the reading in the burette and record it in the Observation Table I under the column 'Initial reading'.

iii) Pipette out 25 cm^3 of test solution in a 250 cm^3 conical flask. Add 10 cm^3 of 0.1 *M* NaOH solution and 3-4 drops of Murexide indicator solution. Dilute it to 50 cm^3 with distilled water. Now titrate with EDTA solution until the colour changes from red to purple. Repeat the titration 3-4 times to obtain concordant values. Record the values in Observation Table I under the column 'Final Reading'. This gives volume (V_1) of EDTA required for calcium ions only.

Solution should be warmed to 50–60°C, but under no circumstances it should be boiled.

iv) Pipette out 25 cm^3 of another portion of the test solution containing both magnesium and calcium ions, in a 250 cm^3 conical flask. Add 5 cm^3 of buffer solution (pH = 10) and dilute it to 50 cm^3 with distilled water. Ensure that the smell of ammonia persists. If necessary add 2-3 drops of liquor ammonia. Add Solochrome Black indicator (3-4 drops) and warm up to 50-60°C. Now, titrate with EDTA solution till the wine red colour of the solution changes to bluish. Note the final reading in the burette and record it in the Observation Table II under the column 'Final reading'. Repeat the titration 3-4 times till concordant values are obtained. This gives the volume (V_2) of EDTA required for both calcium and magnesium ions.

15.5 OBSERVATIONS

Approximate mass of the weighing bottle = m_1 =.............. g

Mass of the weighing bottle + EDTA salt = m_2 =.............. g
(before transferring the salt)

Mass of the weighing bottle = m_3 =.............. g
(after transferring the salt)

Observation Table I
Titration of the test solution with EDTA using Murexide indicator

Sl. No.	Volume of test solution in cm^3	Burette reading Initial	Final	Volume of EDTA salt, V_1 in cm^3 (Final–Initial)
1.	25			
2.	25			
3.	25			
4.	25			

Observation Table II
Titration of the test solution with EDTA using Solochrome Black indicator

Sl. No.	Volume of test solution in cm^3	Burette reading Initial	Final	Volume of EDTA salt, V_2 in cm^3 (Final–Initial)
1.	25			
2.	25			
3.	25			
4.	25			

15.6 CALCULATIONS

Molarity of EDTA salt solution

Mass of EDTA salt transferred $(m) = m_2 - m_3 =$ .... g

Molar mass (M_m) of sodium salt of EDTA = 372.3 g mol^{-1}

Volume of EDTA salt solution prepared = 250 cm^3

$$\text{Molarity of EDTA salt solution} = M_1 = \frac{m \times 1000}{M_m \times 250} \text{ mol dm}^{-3}$$

$$= \frac{m \times 4}{372.31} \text{ mol dm}^{-3}$$

Concentration of Calcium ions in solution

Volume of calcium ion solution = V_2 = 25 cm^3

Molarity of Calcium ion solution = M_2 = ?

Volume of EDTA salt solution required for calcium ions = V_1 cm^3 (From Table I)

$$\text{Molarity of EDTA salt solution} = M_1 = \frac{m \times 4}{372.31}$$

Now, using the molarity equation, $M_1V_1 = M_2V_2$, we get,

$$M_2 = \frac{M_1V_1}{V_2}$$

$$= \frac{m \times 4 \times V_1}{372.31 \times 25} \text{ g dm}^{-3}$$

Hence, concentration of calcium ions = molarity × molar mass of Ca^{2+}

$$= \frac{m \times 4 \times V_1}{372.31 \times 25} \text{ mol dm}^{-3} \times (40.08 \text{ g mol}^{-1})$$

$$= \frac{m \times 4 \times V_1 \times 40.08}{372.31 \times 25} \text{ g dm}^{-3}$$

Concentration of Magensium ions in solution

Volume of magnesium ion solution $= V_3 = 25\ cm^3$

Molarity of magnesium ion solution $= M_3 = ?$

Volume of EDTA salt solution required for magnesium ions $= (V_2 - V_1)\ cm^3$

Molarity of EDTA salt solution $= M_1 = \frac{m \times 4}{372.31}$

Now, using the molarity equation, we get,

$$M_1 (V_2 - V_1) = M_3 V_3$$

or

$$M_3 = \frac{M_1 (V_2 - V_1)}{372.31 \times 25}$$

$$= \frac{m \times 4 \times (V_2 - V_1)}{372.31 \times 25}\ \text{mol dm}^{-3}$$

Hence, concentration of magnesium ions=molarity×moar mass of Mg^{2+}

$$= \frac{m \times 4 \times (V_2 - V_1)}{372.31 \times 25}\ \text{mol dm}^{-3} \times (24.32\ \text{g mol}^{-1})$$

$$= \frac{m \times 4 \times (V_2 - V_1) \times 24.32}{372.31 \times 25}\ \text{g dm}^{-3}$$

15.7 RESULT

You can report your result in the following form:

1. Calcium content in the solution =........... g dm^{-3}
2. Magnesium content in the solution =........... g dm^{-3}