Complex-formation titrations are widely used for determining metallic elements. For most applications, the reagents are organic compounds that contain several electron-donor groups that form stable covalent bonds with metal ions.

Most metal ions react with electron-pair donors to form coordination compounds or complex ions. The donor species, or ligand, must have at least one pair of unshared electrons available for bond formation. Water, ammonia, and halide ions are common inorganic ligands. The ligand which has more than one binding site for a metal ion is known as a chelating agent. The type of complex that forms between a metal ion and a chelating agent is known as chelate. Chelating agents can be divided into various subcategories based on how many binding sites they possess for a metal ion. Chelating agents may have two, three, four and even more sites for binding metals, making them bidentate, tridentate, tetradentate, or polydentate ligands.

Ethylenediaminetetraacetic acid (EDTA) is one of the most widely used chelating agents in quantitative estimation of metals. The structure of EDTA and its complex with a metal ion, Ca$^{2+}$, are shown in the following figure.

The EDTA molecule has six potential sites for bonding a metal ion: the four carboxyl groups and two amino groups, each of the latter with an unshared pair of electrons. Thus, EDTA is a hexadentate ligand. The dissociation constants for the acidic groups in EDTA are $K_1 = 1.02 \times 10^{-2}$, $K_2 = 2.14 \times 10^{-3}$, $K_3 = 6.92 \times 10^{-7}$, and $K_4 = 5.50 \times 10^{-11}$. These values indicate that the first two protons are lost much more readily than the remaining two. Cation-EDTA equilibria are pH dependent and because of this, EDTA titrations are generally carried out in buffered solutions. An alkaline medium is needed for titration involving cations such as calcium and magnesium which form weak complexes with EDTA.

In a titration with EDTA, the formation constant of the metal-indicator complex should be less than one tenth of the metal-EDTA complex, otherwise a premature end point will be observed. On the other hand, if this ratio is too small, late end points are observed. Thus, the choice of indicator is quite important for the success of the experiment.

The abbreviations $H_4Y$, $H_3Y^-$, $H_2Y^{2-}$, $HY^3$ and $Y^4^-$ indicate EDTA molecules with increasing number of dissociated carboxylic acids. The free acid, $H_4Y$, and the dihydrate of the sodium salt, $Na_2H_2Y.2H_2O$, are available in reagent quality. Solutions of EDTA are particularly valuable as titrants because the reagent combines with metal ions in a 1:1 ratio regardless of the charge on the cation.

The equations for the reactions are as follows:

$$Mg^{2+} + H_2Y^{2-} \rightarrow MgY^{3-} + 2 H^+$$
Ca\(^{2+}\) + H\(_2\)Y\(^2-\) → CaY\(^2-\) + 2 H\(^+\)

The end point for Mg\(^{2+}\) determination is sharp with Eriochrome T indicator (forms red complexes with metal ions) and direct titration can be carried out with EDTA, whereas it is not for Ca\(^{2+}\) determination. In the determination of Ca\(^{2+}\) and hardness of water, Ca\(^{2+}\) forms a more stable complex than Mg\(^{2+}\). In this process, an excess of a solution containing EDTA in the form of a Mg complex is introduced. Magnesium ions in the complex are displaced by a chemically equivalent quantity of Ca\(^{2+}\). The following reaction occurs:

Ca\(^{2+}\) + MgY\(^2-\) → CaY\(^2-\) + Mg\(^{2+}\)

The liberated Mg\(^{2+}\) is then titrated with a standard EDTA solution with Eriochrome Black T indicator. This procedure is useful where no satisfactory indicator is available for the metal ion being determined.

In this experiment i) the amount of magnesium ion in an aqueous solution ii) the amount of calcium ion in an aqueous solution iii) hardness of water will be determined by titration with EDTA.

**Experimental**

**Reagents:**

- 0.01 M EDTA solution
- Buffer solution, pH 10
- Eriochrome Black T indicator
- 0.10 M Magnesium / EDTA Solution

**Procedure**

- **Determination of Magnesium by Direct Titration**

Take 10 mL unknown solution given and dilute it to 50.0 mL with distilled water. Add 1 to 2 mL of pH 10 buffer and Eriochrome Black T indicator not more than half of the size of a pea. Titrate with 0.01 M EDTA to a color change from red to pure blue. Express the result of the analysis in terms of mg Mg\(^{2+}\). (Note 1)

- **Determination of Calcium by Displacement Titration**

Take 10 mL unknown solution given and dilute it to 50.0 mL with distilled water. Add approximately 2 mL of pH 10 buffer, 1 mL of Mg/EDTA solution and Eriochrome Black T indicator not more than half of the size of a pea. Titrate with standard 0.01 M EDTA until a color change from red to blue occurs. Report the result as mg Ca in the sample.
- **Determination of Water Hardness**

Take 50 mL of tap water and introduce 2 mL of pH 10 buffer and Eriochrome Black T indicator not more than half of the size of a pea. Titrate the mixture with standard 0.01 M EDTA until the color changes from red to pure blue. (Note 2). Report the result of the analysis in terms of mg of CaCO$_3$/L of water.

**NOTES:**

1. The color change of the indicator is slow in the vicinity of the end point. Care must be taken to avoid over titration.

2. The color change of the indicator is very slow the absence of magnesium is indicated. In this case add 1 to 2 mL of the Mg/EDTA solution before the titration.
Experiment No. 6

COMPLEX FORMATION TITRATIONS WITH EDTA

Determination of Magnesium by Direct Titration
Volume of 0.01 M EDTA used (mL) :.............

Determination of Calcium by Displacement Titration
Volume of 0.01 M EDTA used (mL) :.............

Determination of Water Hardness
Volume of 0.01 M EDTA used (mL) :.............

Submitted by: Submitted to:

Date: