Substitution Titration

Aim: To estimate the amount of Ca(II) ions present in the given solution of $CaCO_3$ using ~N/50 Na_2H_2Y (disodium-EDTA) and Eriochrome Black T as indicator.

Theory:

Substitution Titration: Substitution titrations are used for metal ions that do not react (or react poorly) with a metallochromic indicator, or for metal ions which form EDTA complexes that are more stable than those of other metals such as magnesium and calcium. The metal ions to be determined may be treated with the magnesium complex of EDTA, when the following reaction takes place:

$$M^{2+} + [MgY]^{2-} \rightleftharpoons [MY]^{2-} + Mg^{2+}$$

Colourless — Colourless — Free metal ion

The amount of magnesium ion set free is equivalent to the cation present and can be titrated with a standard solution of EDTA and a suitable metal indicator.

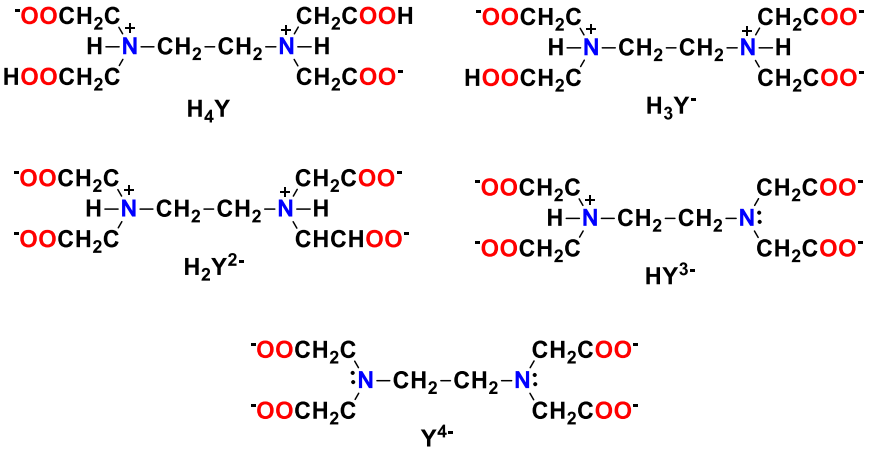


Figure: Chemical drawings of EDTA.

Application of Substitution Titration:

- Titration of Ca^{2+}, Hg^{2+} etc.
- In the direct titration of calcium ions, Eriochrome Black T gives a poor end point; if magnesium is present, it is displaced from its EDTA complex by calcium and an improved end point result.

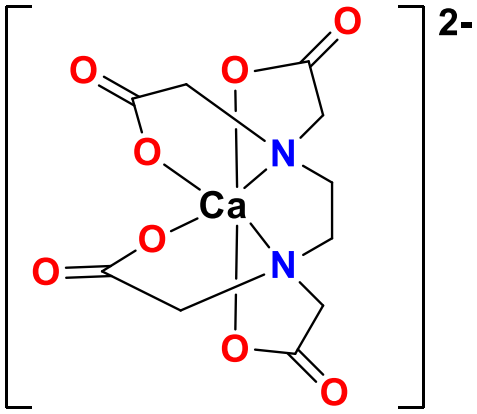
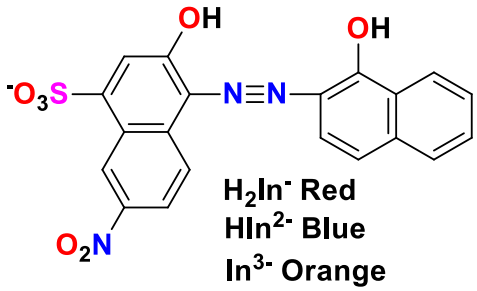


Figure: Chemical drawing of Ca-EDTA complex.

Substitution Titration

Indicator: Eriochrome Black T (EBT)



H_2In^- Red
HIn^{2-} Blue
In^{3-} Orange

$H_2In^- + H_2O \rightleftharpoons HIn^{2-} + H_3O^+$
Red — Blue

$HIn^{2-} + H_2O \rightleftharpoons In^{3-} + H_3O^+$
Blue — Orange

Reaction Mechanism:

In the presence of Buffer solution (NH_3/NH_4Cl): At pH 10

Step 1. $Ca^{2+} + [MgY]^{2-} \longrightarrow [CaY]^{2+} + Mg^{2+}$ (Free metal ion)

K association: Ca-EDTA > Mg-EDTA

Step 2. $H_2In^- + H_2O \rightleftharpoons HIn^{2-} + H_3O^+$
Red — Blue

Step 3. $HIn^{2-} + Mg^{2+} \longrightarrow [Mg\text{-}In]^- + H^+$
Blue — Wine Red

Step 4. $[Mg\text{-}In]^- + H_2Y^{2-} \longrightarrow [Mg\text{-}Y]^{2-} + HIn^{2-}$
Wine Red — Colourless — Blue