Complexometric Titration II

Lecture four 2022-2023

Indicators

- **Indicator** is a dye which is capable of acting as a chelating agent to give a dye-metal complex.
- The latter is different in colour from the dye itself and also **has a low stability constant than the chelate-metal complex**.
- The colour of the solution, therefore, remains that of the dye complex until the end point, when an equivalent amount of sodium EDTA has been added.
- As soon as there is the slightest excess of EDTA, the **metal-dye** complex decomposes to produce free dye; this is accomplished by a change in colour.

Metal indicators must comply with the following requirements:

- Metal-indicator complex must be less stable than the metal-EDTA complex, *ie*. the metal-indicator complex should be 10 to 100 times **less stable** than the metal-titrant complex.
- Binding between metal and indicator must not be too weak. It has to avoid EDTA replacing at the beginning of the titration.
- Colour of the indicator and the metal complexed indicator must be sufficiently different.

EDTA Titration Techniques

- Direct Titration
- Many metals can be determined by direct titrations with EDTA.
- Weak metal complexes such as Ca^{2+} , $Zn^{2+}$and Mg^{2+} should be titrated in basic solution using EBT, *Calmagite, or Arsenazo I* as the indicator.
- Example
- **Direct determination of Zn^{2+} with EDTA**
- The complex of Zn^{2+} with **EDTA (Zn-EDTA)** is **more stable** than its complex with **EBT**.
- $Zn^{2+} + H\text{-}Ind.^{2-} \longrightarrow Zn\text{-}Ind.^{-} + H^{+}$ (conical flask)
- $Zn\text{-}Ind.^{-} + H_2Y^{2-} \longrightarrow ZnY^{2-} + H\ Ind.^{2-} + H^{+}$ (during titration)

wine red **Blue**

EDTA Titration Techniques

- Back Titration (indirect)
- It can be performed for the determination of several metal ions which can not be titrated directly but form stable EDTA complexes.

The procedure, a known amount of EDTA is added to the analyte sample solution and the excess is back titrated with a standard solution of “weak” metal ion, Mg^{2+}.

The weak metal ion will not displace the analyte from its EDTA complex.

It is used in the following cases: (when can be used?)

A. Insoluble substances **e.g.** **$BaSO_4$, CaC_2O_4 , $PbSO_4$, $Mg_3(PO_4)_2$ … etc.** Usually soluble in hot **EDTA.**

B. The reaction between **M^{n+} & EDTA** is slow (incomplete) **e.g.** **Fe^{3+} , Al^{3+} , Cr^{3+} , Th^4 , … etc.**

C. The **M^{n+}** is pptd. at the pH suitable for titration e.g. **$Al(OH)_3$.**

EDTA Titration Techniques

Displacement Titration (what is the conditions??)

A. The technique **only works** when the unknown metal has tighter binding to EDTA than the Zn^{2+} or Mg^{2+}.

B. Metal ions with no satisfactory indicator.

- MgY^{2-} or ZnY^{2-} complex is added to the solution of unknown metal ion composition.
- The unknown metal displaces the Mg^{2+} or Zn^{2+}, which is then back titrated.

$$M^{n+} + MgY^{n-2} \longrightarrow MY^{n-4} + Mg^{2+}$$

K_f' for MY^{n-2} > K_f' for MgY^{n-2}

K_f' is constant of complex formation

Titration of Mixtures

- EDTA is not a selective reagent (it chelates with most metal ions)
- Selectivity of *EDTA* can be increased by one of the following procedures:
  - a) Control of pH of the medium
  - b) Adjustment of oxidation number of metal ion
  - c) Masking and demasking agent

a) Control of pH of the medium

- **First group:** Trivalent & tetravalent cations **e.g.** **(Bi^{3+} , Fe^{3+} , Th^{4+})** and **Hg^{2+}** titrated (form stable complex) at pH 1-3 using conc. **HNO_3**.

- **Second group:** Divalent metals **e.g.** **(Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , pb^{2+}** and **Cd^{2+})** titrated (form stable complex) at pH 4-6 using acetate buffer.

- **Third group:** Alkaline earth metal **e.g.** **(Ba^{2+} , Sr^{2+} , Ca^{2+})** and **Mg^{2+}** titrated (form stable complex) at pH=10 using ammonia buffer or 8% **NaOH**.

- **From the mentioned above**, we can titrate **M^{n+}** of the first group at pH 1-3 without interference of the second and third groups or at pH 4-6 we can titrate **M^{n+}** of the second group without interference of the third group.

- **e.g.** Mixture of **Bi^{3+} & pb^{2+}**: First titrating **Bi^{3+}** at pH = 2 using xylenol orange as ind., then increased pH to 5 by adding hexamine and titrating **pb^{2+}**.

b) Adjustment of oxidation number of metal ion

- This solves the interference between **M^{n+}** of the same group of pH.
- **Examples:**

❖ Ascorbic acid (vit. C) is reducing agent used in:

- Removal of interference of **Fe^{3+}** in first group (pH 1-3) ⟶ reduced to **Fe^{2+}**
- Removal of interference of **Hg^{2+}** in first group (pH 1-3) ⟶ reduced to **Hg^{o}** (pptd.).
- Removal of interference of **Cu^{2+}** in second group (pH 4-6) ⟶ reduced to **cuprous** **Cu^{1+}**.

❖ Oxidation of **Cr^{3+}** $\xrightarrow[H_2O_2]{alkaline}$ to **CrO_4^{2+}**

- **Fe^{2+} , Hg^{o}, Cu^{1+} , CrO_4^{2-}** do not react with **EDTA**

c) Masking and demasking agent

- **Masking agents:** Protects some component of analyte from reacting with EDTA. **These reagents** form complexes with interfering ions which **are more stable than complexes formed with ind. & *EDTA*.**

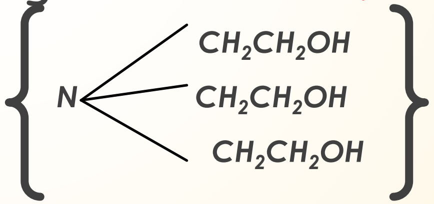
- Examples of masking agent: **(give examples of masking agent)**

KCN: It is used as masking agent for **Ag^+, Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, … etc.**

$$M^+ + 2\ CN^- \longrightarrow [M(CN)_2]^-$$

$$M^+ + 4\ CN^- \longrightarrow [M(CN)_4]^{2-}$$

Triethanolamine: It is used as masking agent for **Fe^{3+}, Al^{3+}** and **Sn^{2+}**



Fluoride (e.g. NH_4F): It is used as masking agent for **Fe^{3+}** and **Al^{3+}** to give $[FeF_6]^{3-}$ and $[AlF_6]^{3-}$

Iodide (KI): It is used as masking agent for **Hg^{2+}** to give tetraiodo complex **(HgI_4)**

- **Demasking agent** : Releasing masking agent from analyte.
- Example of using masking and demasking agents in complexometry is the analysis of 3 metals, Cu, Cd and Ca. the following method of analysis is followed

Step 1: All metals are titrated

$$\begin{matrix} Ca \\ Cd \\ Cu \end{matrix} \quad + \quad EDTA \rightleftharpoons \begin{matrix} Ca\text{-}EDTA \\ Cd\text{-}EDTA \\ Cu\text{-}EDTA \end{matrix}$$

How can we determine a mixture of metals using complexometric titration?

Step 2: Only Ca titrated

$$[Cu, Cd] \quad + \quad \underset{\text{cyanide ion}}{CN^-} \longrightarrow \begin{matrix} [Cu\text{-}cyanide]complex \\ [Cd\text{-}cyanide]complex \end{matrix}$$

$$Ca \quad + \quad \underset{\text{cyanide ion}}{CN^-} \longrightarrow \text{no reaction} \xrightarrow{EDTA} [Ca\text{-}EDTA]$$

- Step 3: Cd and Cu are titrated
- $[\text{Cd-cyanide}]\text{complex} + \text{HCHO} \rightleftharpoons \text{Cd}^{2+}$ (free)
- $[\text{Cu-cyanide}]\text{complex} + \text{HCHO} \longrightarrow$ no reaction

$$\begin{matrix}\text{Cd}\\ \\ \text{Cu}\end{matrix} + \text{EDTA} \overset{\textit{demasking agent}}{\rightleftharpoons} \left\{\begin{matrix}\text{Cd-EDTA}\\ \\ \text{Cu-EDTA}\end{matrix}\right\}$$

Oxidation with H_2O_2 releases Cu^{2+} from $[Cu^{+}\text{-Thiourea}]$ complex.