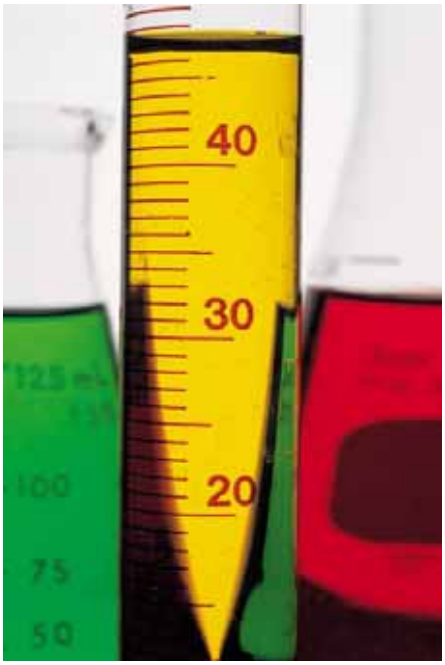
Lecture 3: Complexometric Titrations

July 3, 2006



Purpose

- To learn the principles and techniques of complexometric titration.
- To prepare a standard Zn^{2+} solution.
- To use the latter solution to standardize an EDTA solution.
- To use the standardized EDTA solution for the determination of the amount of Zn^{2+} in an unknown solution.

Theoretical background

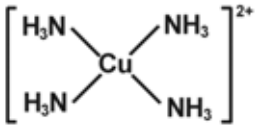
- A complex ion is a chemical species in which a metal atom is bonded to one or more electron-donating groups.
- It is called a coordination compound (because of the coordinate-covalent bond).
- The metal atom or cation is referred to as the central atom.
- The electron-donating group is the ligand.

Types of ligands

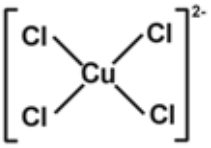
- Based on charge:
  - Neutral: NH_3, $NH_2CH_2CH_2NH_2$, H_2O
  - Negatively charged: Cl^-, OH^-, F^-, CN^-,SCN^-
- Based on number of e^--donating groups (e^- pairs):
  - One pair → monodentate ligand
  - More than one pair → multidentate ligand (bidentate, tridentate,tetradentate,etc…)

Ethylene diamine $H_2N-CH_2-CH_2-NH_2$ A bidentate ligand

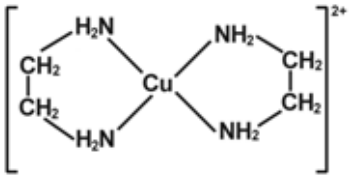
Complex ions



Tetraammine copper (II) ion



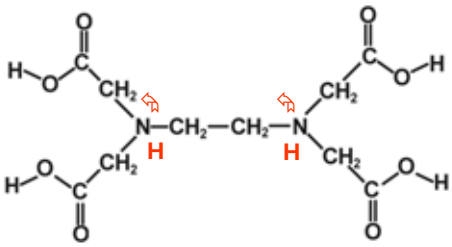
Tetrachloro cuprate (II)



Bis-(ethylenediamine) copper (II) ion

EDTA

- **Most complexometric titrations are carried out with** EDTA**, a hexadentate ligand.**



Ethylene diamine tetra acetic acid

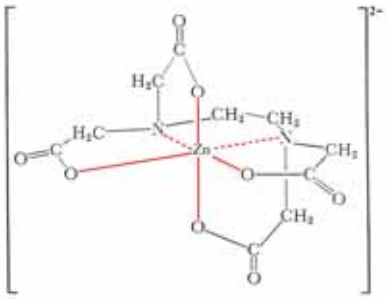
Complexation with EDTA

- **Stoichiometric, instantaneous, reaction:**

$$Zn^{2+} + Y^{4-} \longrightarrow ZnY^{2-}$$

- **Formation constant:**

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]} = 3.2 \times 10^{16}$$

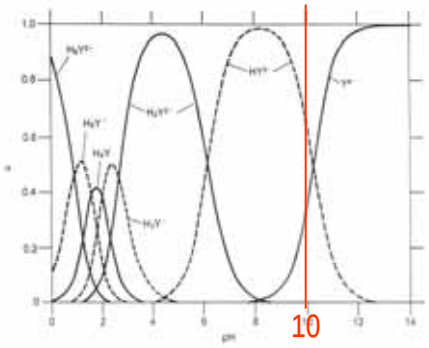


A CHELATE compound

Forms of EDTA at different pH's

- **Six successive ionizations:**

$$H_6Y^{2+} \rightleftharpoons H_5Y^{+} \rightleftharpoons H_4Y \rightleftharpoons H_3Y^{-} \rightleftharpoons H_2Y^{2-} \rightleftharpoons HY^{3-} \rightleftharpoons Y^{4-}$$



Indicator

- **Zn^{2+}, Y^{4-} and ZnY^{2-} are all colorless.**
- **We use an indicator which complexes with Zn^{2+}, Eriochrome Black T (Erio-T).**
- **Erio-T is a <u>triprotic acid</u>:**

$$H_3E \rightleftharpoons H_2E^- \rightleftharpoons HE^{2-} \rightleftharpoons E^{3-}$$

predominant at pH 10.0

Reaction in the presence of Erio-T

- **It is convenient to carry out the reaction at pH =10.0 (we use an NH_3/NH_4Cl buffer).**
- **Erio-T complexes with Zn^{2+} at pH 10.0**

$$Zn^{2+} + HE^{2-} \longrightarrow ZnE^- + H^+$$

blue — wine red

- Reaction with EDTA:

$$ZnE^- + HY^{3-} \longrightarrow ZnY^{2-} + HE^{2-}$$

wine red — blue

at $[Zn^{2+}]<10^{-8}$ M

Procedure and report

- *Procedure*
- *Report*
- *Assigned questions:* 1, 2 and 4 (think about Q. 3).

Applications

- Determination of the hardness of water (notably in Ca^{2+}).
- Determination of the %Ca content in egg shells.
- Etc.