Pharmaceutical analysis I BP102TP

COMPLEXOMETRIC TITRATION

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Complexometric titrations

Complexometry

- **A titration based on the formation of a coordination complex is known as a complexometric titration.**

➢ **Complex formation titrations are used to titrate cations via complex formation reagents.**

➢ **Most, if not all, metals form coordination complexes with anions or molecules. For example,**

$$Fe^{2+} + 6\ CN^{1-} \rightarrow Fe(CN)_6^{4-}$$

➢ **Molecules/anions that react with metal ions must donate an unshared pair of electrons to form a coordinate covalent bond**

- **Molecules composed of metals and chelates or metals and coordinating agents are known as coordination complexes.**
- **Chelating agents form strong 1:1 complexes with metal ions.**
- **Most common chelating agents belong to a group of compounds called polyaminocarboxylic acids.**

The complex can form only when…

1. The central atom *(a metal ion (or cation) in a complex)* accepts an electron pair from one or more ligands *(ligand = electron-pair donating species)*.

2. The ligand possesses at least one electron pair to donate.

3. The bonding (coordinate covalent bonding) occurs .

A number of common anionic and molecular ligands can form complexes:

1. Anionic ligands include halides, SCN^{1-}, CN^{1-}, OH^{1-}, $RCOO^{1-}$, S^{2-}, $C_2O_4^{2-}$ (oxalate), etc.

2. Molecular ligands include water, ammonia, RNH_2 (amines) C_5H_5N (pyridine) $H_2NCH_2CH_2NH_2$ (ethlenediamine), etc.

Ligands that have (or share) only one electron pair are called unidentate.

1. "Dentate" = a tooth-like projection.

2. For example, ammonia is unidentate...

$$Cu^{2+} + 4\ NH_3 \qquad Cu(NH_3)_4^{2+}$$

Bidentate ligands share two electron pairs. Examples:

1. Glycine complexed with copper(II).

2. Ethylenediamine complexed with zinc ion.

Multidentate ligands complexed to metal ions are called chelates. Chelates always have a "chelate ring." For example, the zinc-8-hydroxyquinolate complex.

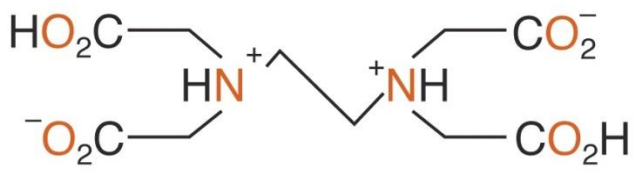
Complex Formation Titrations

The most commonly used chelon (or titrant) in metal ion titrations is EDTA (ethylenediaminetetracetic acid).

EDTA

- **Ethylene diamine tetraacetic acid. $H_4EDTA \Rightarrow H_4Y$**
  - **ethylenediaminetetraacetate anion**

⇨ $EDTA^{-4} \Rightarrow Y^{-4}$



EDTA
Ethylenediaminetetraacetic acid
(also called ethylenedinitrilotetraacetic acid)

EDTA is hexadentate, donating one electron pair from each of the two amine group and one electron pair from each of the four carboxylates to the bound metal ion.

- **Virtually every element in the periodic table can be determined by titrating with EDTA.**
- **EDTA forms a "cage" around metal ions, like a spider grasping a fly.**
- **Note that *only the fully ionized, -4-charged anion binds to metal ions.***
- **Competition of the metal ion with protons dictates that the solution must be well buffered.**
- **EDTA is used as a titrant for the determination of water hardness.**
- **EDTA is a tetraprotic acid,**

Standard solutions of EDTA are usually prepared by dissolving the $Na_2H_2Y{\cdot}2H_2O$ in a volumetric flask. (Note: Most $Na_2H_2Y{\cdot}2H_2O$ at normal, atmospheric conditions comes with 0.3% excess water in the crystal. The excess water must be taken into account when preparing standard solutions.)

Colorimetric indicators

- Also known as metallochromic indicators.
- The color change occurs when the metal ion is bound with the indicator.
- This binding is pH dependent.
- Masking agents are often used for complexometric titrations, which allow for the removal of interferents.

Metal Ion Indicators

- Over 200 organic compounds form colored chelates with ions in a pM range that is unique to the cation and the dye selected.
- To be useful, the dye-metal chelates usually will be visible at 10^{-6}-10^{-7} M concentration.

The dye is selected such that the color change corresponds to the pM at equivalence.

Examples:

Erichrome Black T

- **Eriochrome Black T is an azo dye, best used with Mg^{2+} and Zn^{2+} titrations.**
- **Excess EDTA causes a red to blue color change at near neutral pH.**
- **Eriochrome Black solutions decompose easily.**

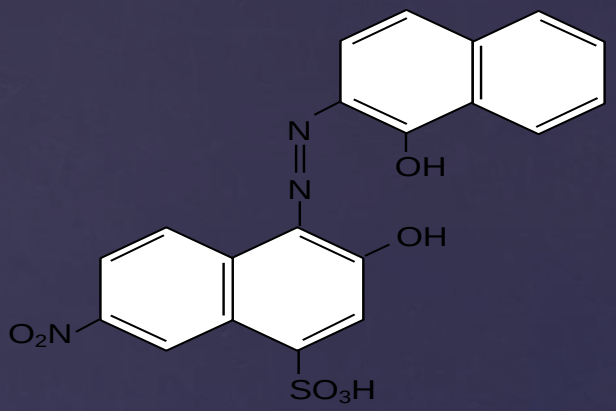
MgIn + EDTA → MgEDTA + In

(red) (colorless) (blue)

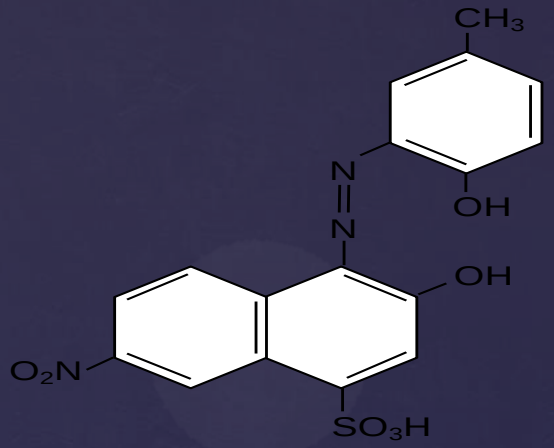
Calmagite/calgamite

- **Similar in structure to Eriochrome Black but does not decompose as easily.**
- **Similar color behavior to Eriochrome Black and more stable.**

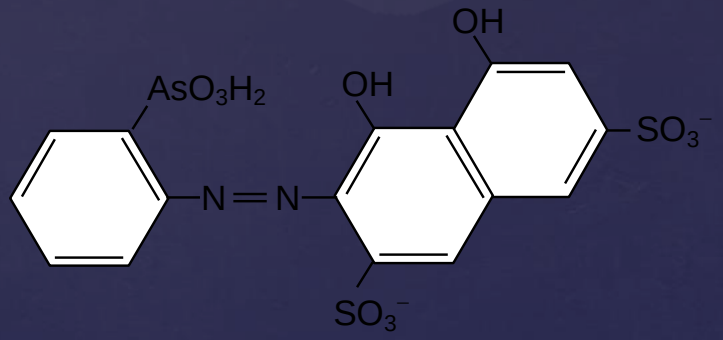
Common indicators for complexometric titrations



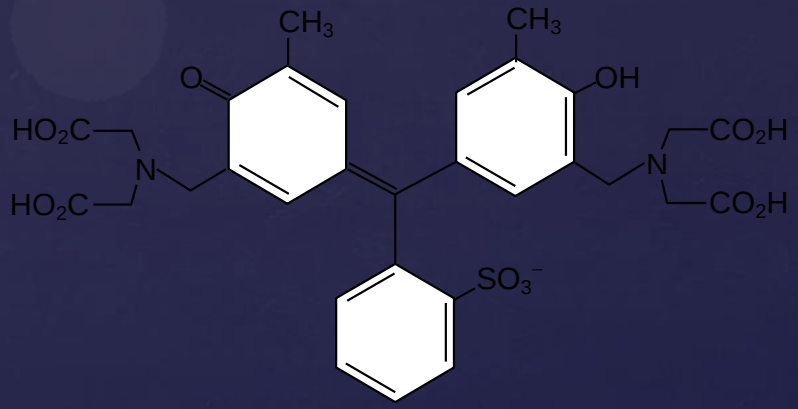
Eriochrome Black T



Calgamite



Arsenazo I



Xylenol Orange

EDTA Titration

EDTA combined with the metal ion (1 : 1) to form complex.

For a +1 cation: $Ag^{+} + Y^{4-} \rightarrow AgY^{3-}$

For a +2 cation: $Hg^{2+} + Y^{4-} \rightarrow HgY^{2-}$

For a +3 cation: $Fe^{3+} + Y^{4-} \rightarrow FeY^{-}$

For a + n ion: $M^{n+} + Y^{4-} \rightarrow MY^{(n-4)+}$

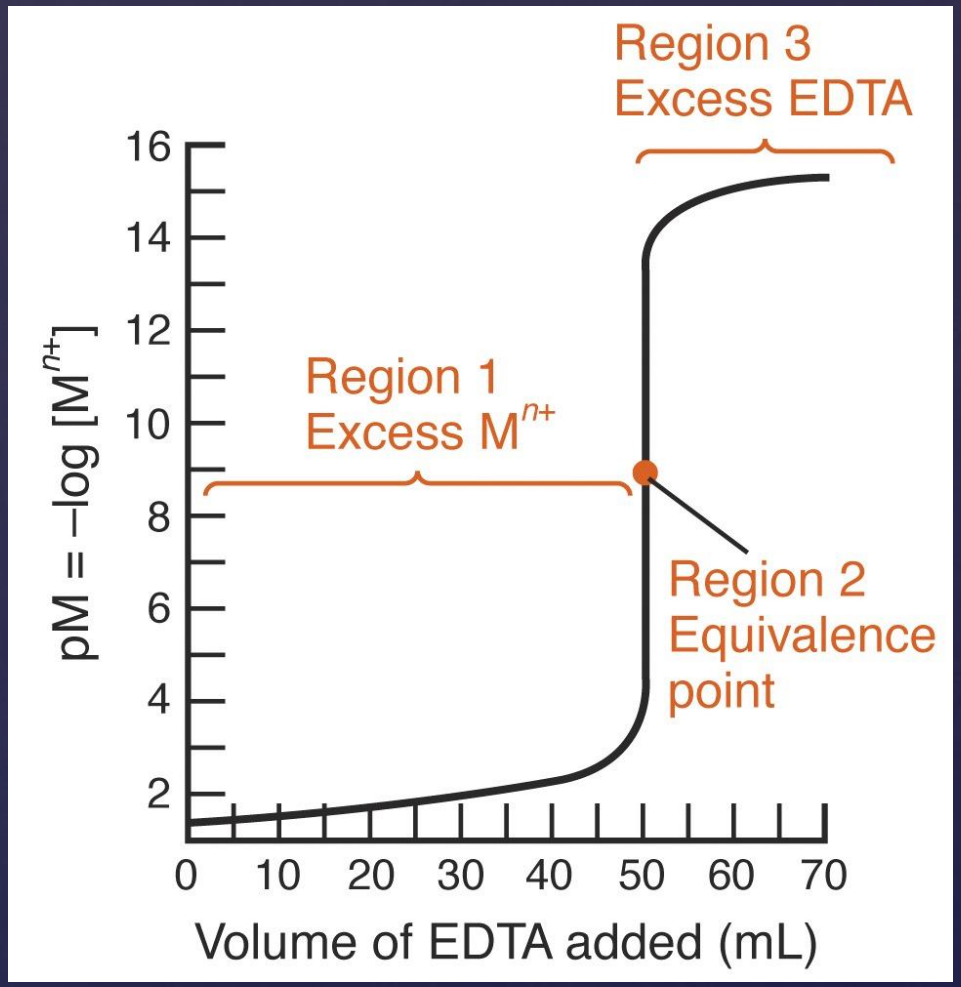
The Formation Constant,

$$K_{MY} = \frac{[MY^{(n-4)+}]}{[M][Y^{4-}]}$$

Three Regions of EDTA Titration

The curves are easily calculated by dividing the curve up into domains:

- **The pM before equivalence.**
- **The pM at equivalence.**
- **The pM after equivalence.**



EDTA Titration Techniques

Direct Titration

- Many metals can be determined by direct titrations with EDTA.
- Weak metal complexes such as Ca^{2+} and Mg^{2+} should be titrated in basic solution using EBT, Calmagite, or Arsenazo I as the indicator.

example

A 100.0 mL drinking water containing Ca^{2+} was treated with ammonia-ammonium chloride buffer solution to give pH about 10.0. Calgamite indicator was added and the solution was titrated with 0.0050 M EDTA. It required 23.50 mL of the titrant to achieve the end point. Calculate the water hardness in terms of ppm calcium?

EDTA Titration Techniques

Back Titration

- Back titration can be performed for the determintion of several metal ions 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.
- Calgamite can be used as an indicator for the back titration of the excess EDTA with standard magnesium ion solution.

Example

A 20.00 mL of a solution containing Hg^{2+} in dilute nitric acid was treated with 10.00 mL of 0.0500 M EDTA and the solution was added with ammonia-ammonium chloride buffer solution to a give pH of 10. A few drops of freshly prepared EBT indicator was added and the excess EDTA was back titrated with 0.0100 M Mg^{2+}. It required 25.50 mL of the titrant to reach the end point. Calculate the molariy of Hg^{2+} in the sample.

Displacement Titration

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