Chapter 13: EDTA titrations

Complexation Reaction: A reaction between two species having a well-defined stoichiometry. The resulting bond is not permanent from a covalent standpoint.

Complex: The resulting structure formed during a complexation reaction.

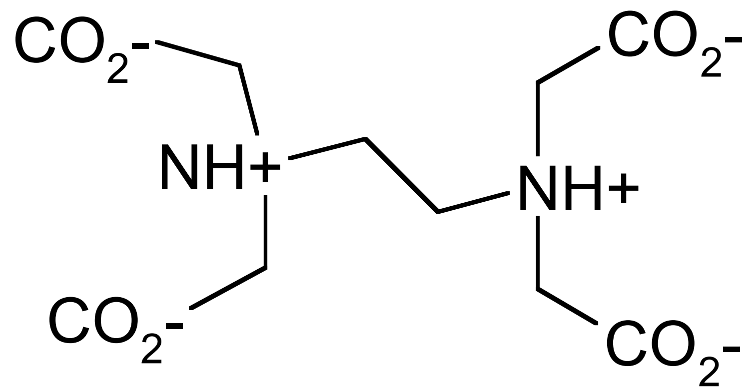
Coordination Center: Metal ion in a complex (Lewis acid)

Ligand: The species that complexes the metal center. A single species can form one or more bonds with a single coordination center (Lewis base)

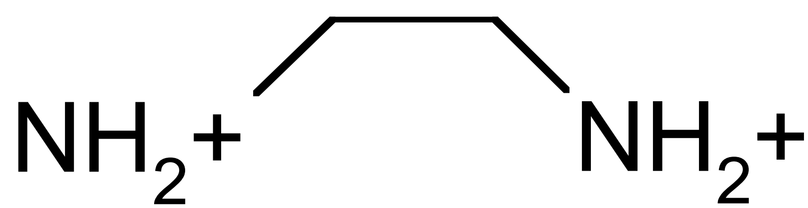
Coordination Number: Number of ligand bonds formed around the coordination center.

Chelate: Ligands that form multiple bonds (multidentate; bi, tri, tetra, penta)

Ethylenediaminetetraacetic acid
EDTA



Ethylenediamine

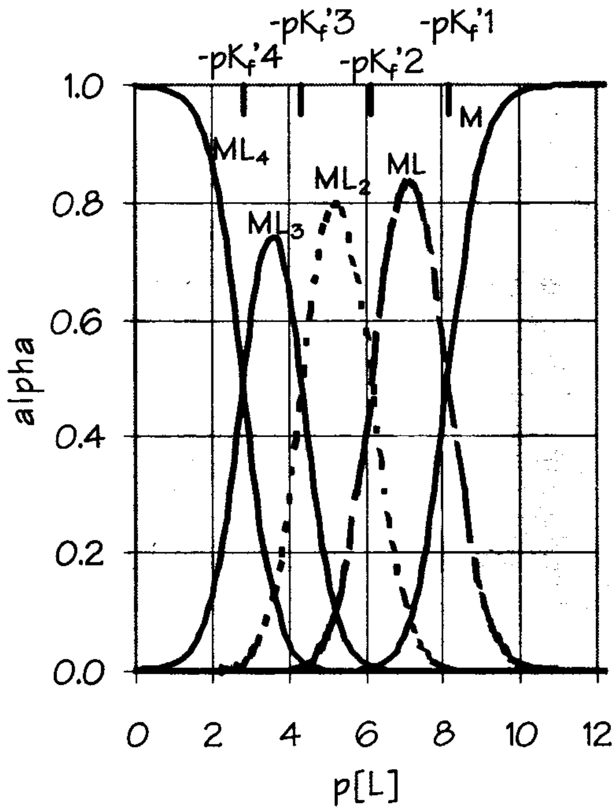


- EDTA is the most commonly used chelating agents as it can form complexes with a wide range of metals.
- The ability of EDTA to complex is dependent on its form. The most desirable state is the Y^{4-} form.
- As the pH increases, more EDTA becomes Y^{4-}.

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[H_6Y^{2+}]+[H5Y^{+}]+[H_4Y]+[H_3Y^{-}]+[H_2Y^{2-}]+[H\ Y^{3-}]+[Y^{4-}]}$$

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[EDTA]}$$

Equil. Concentrations



- The formation constant for metal-EDTA complexes is:

$$M^{n+} + Y^{4-} = MY^{n-4} \quad K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]}$$

- It is important to note the requirement for the charge state of EDTA. Leads to a conditional (effective) formation constant

$$K'_f = \alpha_{Y^{4-}} K_f = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$$

Equilibrium Concentrations

- Again we must consider equilibrium reactions and concentrations in analysis using complexation.
- Equilibrium constants are referred to as formation constants, K_f.
- For simple complexes (1:1) we can make some similar assumptions and generate similar equations as we did for monoprotic acids
- For more complex systems we must deal with **step-wise formations** and **step-wise formation constants**.

EDTA titrations

1. Before the equivalence point there is excess M in solution
2. At the equivalence point, treated as dissolving pure MY complex.
3. After equivalence there is excess EDTA

Indicators

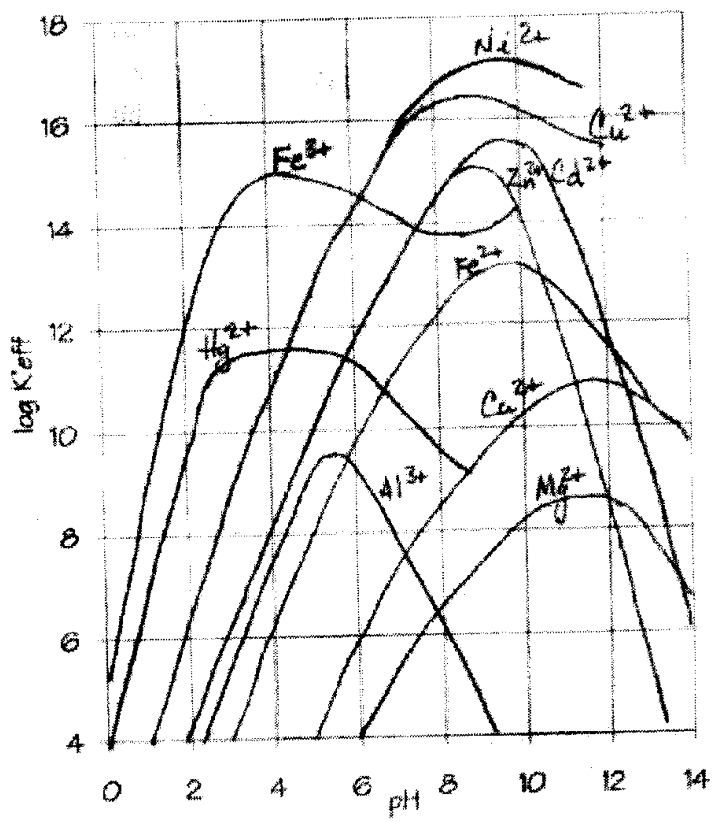
- The most common indicator is the metal ion indicator
  - To be useful must bind less strongly than EDTA
  - The most common indicator is Eriochrome black T. EBT binds to metal ions to give a red color. Upon release of the metal to EDTA, it becomes blue
- Can use ion specific electrodes and/or mercury electrodes. Both of these are more expensive and time consuming.

Sometimes there is not a strong reaction between EBT and the metal. This can be overcome by a **displacement titration**. The solution begins with the Mg^{2+} complexed with EDTA. The analyte is added (assuming higher binding constant and lower concentration) and the Mg^{2+} is displaced. The Mg^{2+} is titrated with EBT.

A second way to overcome titrations with weak end points is to do a **back titration**. In a back titration, excess EDTA is added to the sample solution. The excess is then titrated with a standard Mg or Zn solution.

EDTA is a widely applicable complexing agent as it will complex with almost any metal. This can be a problem if selectivity is desired however.

Selectivity can be controlled through pH.



A second method for adding selectivity is to add a competing reagent called a **masking agent**.

A masking reagent reacts with one of the species and allows titration of the second. This can be applied to a simple binary mixture or to a more complex mixture.

For example, if NH_3 is used as a buffer, Cd^{2+} can be titrated in the presence of Zn^{2+}.