

جامعة الانبار

كلية : الصيدلة

قسم : الكيمياء الصيدلانية

اسم المادة باللغة العربية: الكيمياء التحليلية

اسم المادة باللغة الإنكليزية: **Analytical Chemistry**

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عنوان المحاضرة باللغة العربية: تسحيحات تكوين المعقدات

عنوان المحاضرة باللغة الإنكليزية : **Complex -Formation Titration**

#### 8.4 Organic Complexing Agents

Many different organic complexing agents have become important in analytical chemistry because of their inherent sensitivity and potential selectivity in reacting with metal ions. Such reagents are particularly useful in precipitating metals, in binding metals to prevent interferences, in extracting metals from one solvent to another, and in forming complexes that absorb light for spectrophotometric determinations. The most useful organic reagents form chelate complexes with metal ions.

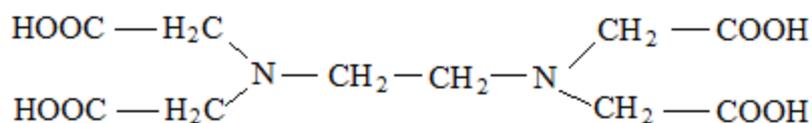
Many organic reagents are used to convert metal ions into forms that can be readily extracted from water into an immiscible organic phase as shown in Table 8-1.

**Table 8-1 Organic Reagents for Extracting Metals**

Reagent	Metal Ions Extracted	Solvents
8-Hydroxyquinoline	$Zn^{2+}$ , $Cu^{2+}$ , $Ni^{2+}$ , $Al^{3+}$	Water $\rightarrow$ $CHCl_3$
Diphenylthiocarbazone	$Cd^{2+}$ , $Co^{2+}$ , $Cu^{2+}$ , $Pb^{2+}$	Water $\rightarrow$ $CHCl_3$ , or $CCl_4$
Acetylacetone	$Fe^{3+}$ , $Cu^{2+}$ , $Zn^{2+}$ , U(VI)	Water $\rightarrow$ $CHCl_3$ , $CCl_4$ , or $C_6H_6$
Ammonium pyrrolidine dithiocarbamate	Transition metals	Water $\rightarrow$ Methyl isobutyl ketone

\* *Ethylenediaminetetraacetic acid (EDTA)*

It is the most widely used complexometric titrant. EDTA has the structural formula:



The EDTA molecule has six potential sites for bonding a metal ion: the four carboxylic groups and the two amino groups, each of the latter with an unshared pair of electrons. Thus, EDTA is a hexadentate ligand.

The dissociation constants for the acidic groups in EDTA are  $K_1 = 1.02 \times 10^{-2}$ ,  $K_2 = 2.14 \times 10^{-3}$ ,  $K_3 = 6.92 \times 10^{-7}$ , and  $K_4 = 5.50 \times 10^{-11}$ . It is of interest that the first two constants are of the same order of magnitude, which suggests that the two protons involved dissociate from opposite ends of the rather long molecule. As a consequence of their physical separation, the negative charge created by the first dissociation does not greatly affect the removal of the second proton. The same cannot be said for the dissociation of the other two protons, however, which are much closer to the negatively charged carboxylate ions created by the initial dissociations.

The various EDTA species are often abbreviated  $\text{H}_4\text{Y}$ ,  $\text{H}_3\text{Y}^-$ ,  $\text{H}_2\text{Y}^{2-}$ ,  $\text{HY}^{3-}$ , and  $\text{Y}^{4-}$ .

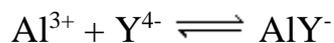
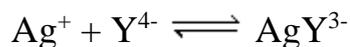
#### **\* Reagents for EDTA titration**

The free acid  $\text{H}_4\text{Y}$  and the dihydrate of the sodium salt,  $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$ , are commercially available in reagent quality. The former can serve as a primary standard after it has been dried for several hours at  $130^\circ\text{C}$  to  $145^\circ\text{C}$ . It is then dissolved in the minimum amount of base required for complete solution.

#### **\* Complexes of EDTA and metal ions**

Solutions of EDTA are particularly valuable as titrants because the reagent combines with metal ion in a 1:1 ratio regardless of the charge

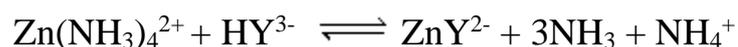
on the cation. For example, the silver and aluminum complexes are formed by the reactions:



EDTA is a remarkable reagent not only because it forms chelates with all cations except alkali metals but also because most of these chelates are sufficiently stable for titrations. This great stability result from the several complexing sites within the molecule that give rise to a cage-like structure, in which the cation is surrounded by and isolated from solvent molecules.

**\* *Effect of other complexing agents on EDTA***

Many EDTA titrations are complicated by the tendency on the part of the ion being titrated to precipitate as a basic oxide or hydroxide at the pH required for satisfactory titration. In order to keep the metal ion in solution, particularly in the early stage of the titration, it is necessary to include an auxiliary complexing agent. Thus, for example, the titration of zinc(II) is ordinary performed in the presence of high concentrations of ammonia and ammonium chloride. These species buffer the solution to an acceptable pH. In addition, the ammonia prevents precipitation of zinc hydroxide by forming ammine complexes. The titration reaction with EDTA is thus best represented as:



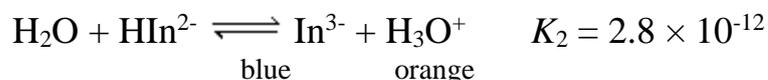
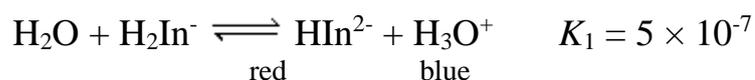
The solution also contains such other zinc/ammonia species as  $\text{Zn}(\text{NH}_3)_3^{2+}$ ,  $\text{Zn}(\text{NH}_3)_2^{2+}$ , and  $\text{Zn}(\text{NH}_3)^{2+}$ . Calculation of pZn in a solution that contains ammonia must take these species into account. Qualitatively, complexation of a cation by an auxiliary complexing

reagent causes preequivalence pM values to be larger than in a comparable solution with no such reagent.

**\* Indicators for EDTA titrations**

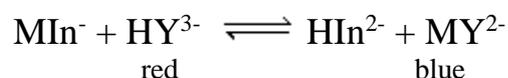
Nearly 200 organic compounds have been investigated as indicators for metal ions in EDTA titrations. In general these indicators are organic dyes that form colored chelate with metal ions in a pM range that is characteristic of the particular cation dye. The complexes are often intensely colored and are discernible to the eye at concentrations in the range of  $10^{-6}$  to  $10^{-7}$  M.

Eriochrome Black T is a typical metal ion indicator that is used in the titration of several common cations. Its behavior as a weak acid is described by the equations:



Note that the acids and their conjugate bases have different colors. Thus, Eriochrome Black T behaves as an acid-base indicator as well as a metal ion indicator.

The metal complexes of Eriochrome Black T are generally red, as is  $\text{H}_2\text{In}^-$ . Thus, for metal ion detection, it is necessary to adjust the pH to 7 or above so that the blue form of the species,  $\text{HIn}^{2-}$ , predominates in the absence of a metal ion. Until the equivalence point in a titration, the indicator complexes the excess metal ion so that the solution is red. With the first slight excess of EDTA, the solution turns blue as a consequence of the reaction:



Eriochrome Black T forms red complexes with more than two dozen metal ions, but the formation constant of only a few are appropriate for end point detection.

### ***8.5 The Scope of EDTA Titrations***

Complexometric titrations with EDTA have been applied to the determination of virtually every metal cation, with the exception of the alkali metal ions. Because EDTA complexes most cations, the reagent might appear at first glance to be totally lacking in selectivity. In fact, however, considerable control over interferences can be realized by pH regulation. For example, trivalent cations can usually be titrated without interference from divalent species by maintaining the solution at a pH of about 1. At this pH, the less stable divalent chelates do not form to any significant extent, but the trivalent ions are quantitatively complexed.

Similarly, ions such as cadmium and zinc, which form more stable EDTA chelate than does magnesium, can be determined in the presence of the latter ion by buffering the mixture to a pH of 7 before titration. Eriochrome Black T serves as an indicator for the cadmium or zinc end points without interference from magnesium because the indicator chelate with magnesium is not formed at this pH.

Finally, interference from a particular cation can sometimes be eliminated by adding a suitable masking agent, an auxiliary ligand that preferentially forms highly stable complexes with the potential interfering ion. Thus, cyanide ion is often employed as a masking agent to permit the titration of magnesium and calcium ions in the presence of ions such as cadmium, cobalt, copper, nickel, zinc, and palladium. All of the latter form sufficiently stable cyanide complexes to prevent reaction with EDTA

## 8.6 *The Determination of Water Hardness*

The simple definition of water hardness is the amount of dissolved calcium and magnesium in the water. Hard water is high in dissolved minerals, largely calcium and magnesium. Depending on the hardness of your water, after using soap to wash you may have felt like there was a film of residue left on your hands. In hard water, soap reacts with the calcium (which is relatively high in hard water) to form soap scum. When using hard water, more soap or detergent is needed to get things clean. Hardness is caused by compounds of calcium and magnesium, and by a variety of other metals. General guidelines for classification of waters are: 0 to 60 mg/L (milligrams per liter) as calcium carbonate is classified as soft; 61 to 120 mg/L as moderately hard; 121 to 180 mg/L as hard; and more than 180 mg/L as very hard. The determination of hardness is a useful analytical test that provides a measure of the quality of water for household and industrial uses. The test is important to industry because hard water, on being heated, precipitates calcium carbonate, which clogs boilers and pipes.

EDTA form a chelated soluble complex when added to a solution of certain metal cations. If a small amount of a dye such as Eriochrome black T is added to an aqueous solution containing calcium and magnesium ions at a pH of 10 (using ammonia as a buffer solution), the solution will become wine red. If EDTA is then added as a titrant, the calcium and magnesium will be complexed. After sufficient EDTA has been added to complex all the magnesium and calcium, the solution will turn from wine red to blue. This is the end point of the titration.



$$\frac{\text{M.wt}_{\text{CaCO}_3}}{\text{Hardness as CaCO}_3 \text{ in ppm (mg/L)}} = \frac{(M_{\text{EDTA}} \times V_{\text{EDTA}}) \times 1000 \times}{V_{\text{water sample}}}$$

The hardness can also be calculated as  $\text{MgCO}_3$