Lecture- 11

Titrations Based on Complexation Reactions

Introduction

    Complexation ractions are important in many areas of science. Complexes play an important role in many chemical and biochemical process. For example the heme molecule in blood holds the iron atom tightly because the nitrogen of the heme form strong complexing bonds, that is nitrogen is a good complexer. Complextion reactions are widely used in analytical chemistry. One of the first uses of these reactions was for titrating cations.

    Most metal ions react with electron-pair donors to form coordination compounds or complexes. The donor species, or **ligand** must have at least one pair of unshared electrons available for bond formation.

    A ligand is an ion or molecule that forms a covalent bond with a cation or neutral metal atom by donating a pair of electrons, which are then shared by the two. Ligands can be classified into inorganic ligands such as water, ammonia, and halide ions, and organic ligands such as 8-hydroxyquinoline.

    The widely compounds (ligands) used in complexemetric titrations called **chelates**. A chelate is produced when a metal ion coordinates with two or more doner groups of a single ligand to form a five or six member heterocyclic ring. A ligand that has:
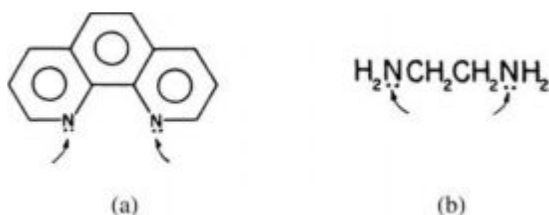
single donor group is called **unidentate**
two donor groups is called **bidentate**
three donor groups is called **tridentate**
four donor groups is called **tetradentate**
five donor groups is called **pentadentate**
six donor groups is called **hexadentate**

(a)   (b)

Two bidentate ligands: (a) 1,10 phenanthroline, and (b) ethylenediamine. The arrows point out the bonding sites.

    Tetradentate and hexadentate ligands are more satisfactory as titrants than ligands with a lesser number of donor groups because their reactions with cations are more complete and because they tend to form 1:1complexes.

### Aminocarboxylic acid titration

    Aminocarboxylic acid compounds are multidentate ligands capable of forming stable 1:1 complexes with metal ions. The most widely used of the new ligands was ethylendiaminetetraacetic acid EDTA which is a hexadentate ligand

and the most important and widely used reagent in titrimetry. The advantages of EDTA is
1- form strong 1:1 complexes.
2- react with many metal ions.

Chemistry and Properties of EDTA

The structure of EDTA is shown in below. EDTA, which is a Lewis acid, has six binding sites (the four carboxylate groups and the two amino groups), providing six pairs of electrons.
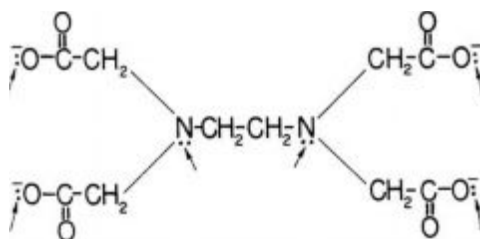

The resulting metal-ligand complex, in which EDTA forms a cage-like structure around the metal ion is very stable. The actual number of coordination sites depends on the size of the metal ion; however, all metal-EDTA complexes have a 1:1 stoichiometry.
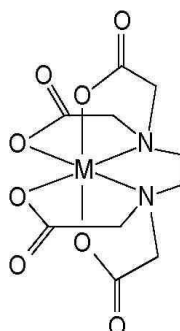
six-coordinate metal-EDTA complex.

Metal—EDTA Formation Constants

To illustrate the formation of a metal-EDTA complex consider the reaction between Cd^{2+} and EDTA

$$Cd^{2+}{}_{(aq)} + Y^{4-}{}_{(aq)} = CdY^{2-}{}_{(aq)}$$
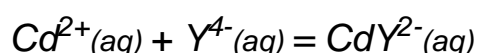
where Y_{4-} is a shorthand notation for the chemical form of EDTA. The formation constant for this reaction

$$K_f = \frac{[CdY^{2}]}{[Cd^{2+}][Y^{4}]} = 2.9 \times 10^{16}$$

is quite large, suggesting that the reaction's equilibrium position lies far to the right.

EDTA Is a Weak Acid
Besides its properties as a ligand, EDTA is also a weak acid. The fully
protonated form of EDTA, H_6Y^{2+}, is a hexaprotic weak acid with successive pK_a
values of
$pK_{a1} = 0.0$ $pK_{a2} = 1.5$ $pK_{a3} = 2.0$ $pK_{a4} = 2.68$ $pK_{a5} = 6.11$ $pK_{a6} = 10.17$
The first four values are for the carboxyl protons, and the remaining two values
are for the ammonium protons.

A ladder diagram for EDTA is shown below.
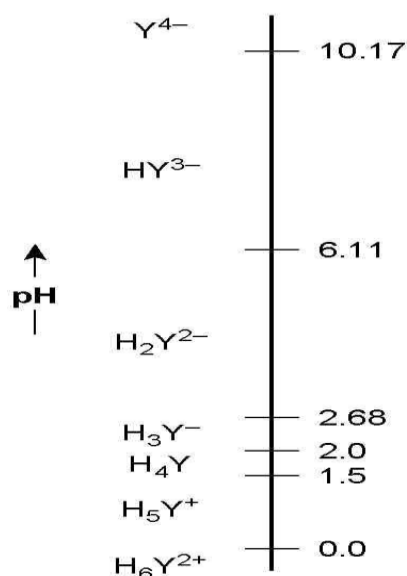
The species Y^{4-} becomes the predominate form of EDTA at pH levels greater
than 10.17. It is only for pH levels greater than 12 that Y^{4-} becomes the only
significant form of EDTA.

Conditional Metal—Ligand Formation Constants
Recognizing EDTA's acid-base properties is important. The formation constant
for CdY^{2-} assumes that EDTA is present as Y^{4-}. If we restrict the pH to levels
greater than 12, then equation

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}][Y^{4-}]} = 2.9 \times 10^{16}$$

provides an adequate description of the formation of CdY^{2-}. For pH levels less
than 12, however, K_f overestimates the stability of the CdY^{2-} complex. At any pH
a mass balance requires that the total concentration of unbound EDTA equal the
combined concentrations of each of its forms.

$C_{EDTA} = [H_6Y^{2+}] + [H_5Y^+] + [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$

To correct the formation constant for EDTA's acid-base properties, we must account for the fraction, $\alpha_{Y^{4-}}$, of EDTA present as Y^{4-}.

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

Values of $\alpha_{Y^{4-}}$ for selected PHs

pH	$\alpha_{Y^{4-}}$	pH	$\alpha_{Y^{4-}}$
2	3.7×10^{-14}	8	5.4×10^{-3}
3	2.5×10^{-11}	9	5.2×10^{-2}
4	3.6×10^{-9}	10	0.35
5	3.5×10^{-7}	11	0.85
6	2.2×10^{-5}	12	0.98
7	4.8×10^{-4}	13	1.00

Solving equation

$$K_f = \frac{[CdY^{2}]}{[Cd^{2+}][Y^{4}]} = 2.9 \times 10^{16}$$

for $[Y^{4-}]$ and substituting gives

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\, \alpha_Y{}^{4-}\, C_{EDTA}}$$

If we fix the pH using a buffer, then $\alpha_{Y^{4-}}$ is a constant. Combining $\alpha_{Y^{4-}}$ with K_f gives

$$K_f^{'} = \alpha_Y{}^{4-} \times K_f = \frac{[CdY^{2}]}{[Cd^{2+}]\, C_{EDTA}}$$

where $K_f{}'$ is a **conditional formation constant** whose value depends on the pH. As shown in following table for CdY^{2-},

pH	K_f'	pH	K_f'
2	1.1×10^3	8	1.6×10^{14}
3	7.3×10^5	9	1.5×10^{15}
4	1.0×10^8	10	1.0×10^{16}
5	1.0×10^{10}	11	2.5×10^{16}
6	6.4×10^{11}	12	2.8×10^{16}
7	1.4×10^{13}	13	2.9×10^{16}

the conditional formation constant becomes smaller, and the complex becomes less stable at lower pH levels.

EDTA Must Compete with Other Ligands
To maintain a constant pH, we must add a buffering agent. If one of the buffer's components forms a metal-ligand complex with Cd^{2+}, then EDTA must compete with the ligand for Cd^{2+}. For example, an NH_4^+/NH_3 buffer includes the ligand NH_3, which forms several stable Cd^{2+}-NH_3 complexes. EDTA forms a stronger complex with Cd^{2+} and will displace NH_3. The presence of NH_3, however, decreases the stability of the Cd^{2+}-EDTA complex.

We can account for the effect of an **auxiliary complexing agent,** such as NH_3, in the same way we accounted for the effect of pH. Before adding EDTA, a mass balance on Cd^{2+} requires that the total concentration of Cd^{2+}, C_{cd}, be

$$C_{cd} = [Cd^{2+}] + [Cd(NH_3)^{2+}] + [Cd(NH_3)_2^{2+}] + [Cd(NH_3)_3^{2+}] + [Cd(NH_3)_4^{2+}]$$

The fraction**,** α_{cd}^{2+} present as uncomplexed Cd^{2+} is

$$\alpha_{cd}^{2+} = \frac{[Cd^{2+}]}{C_{cd}}$$

Solving equation

$$K_f' = \alpha_Y^{4-} \times K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\, C_{EDTA}}$$

for $[Cd^{2+}]$ and substituting gives

$$K_f' = \alpha_Y^{4-} \times K_f = \frac{[CdY^{2-}]}{\alpha_{cd}^{2+}\, C_{cd}\, C_{EDTA}}$$

If the concentration of NH_3 is held constant, as it usually is when using a buffer, then we can rewrite this equation as

$$K_f^{''} = \alpha_{cd}^{2+} \times \alpha_Y^{4-} \times K_f = \frac{[CdY^{2-}]}{C_{cd} \, C_{EDTA}}$$

where $K_f^{''}$ is a new conditional formation constant accounting for both pH and the presence of an auxiliary complexing agent. Values of α_{Mn+} for several metal ions are provided in following table

[NH$_3$] (M)	α_{Ag^+}	$\alpha_{Ca^{2+}}$	$\alpha_{Cd^{2+}}$	$\alpha_{Co^{2+}}$	$\alpha_{Cu^{2+}}$	$\alpha_{Mg^{2+}}$	$\alpha_{Ni^{2+}}$	$\alpha_{Zn^{2+}}$
1	1.00×10^{-7}	5.50×10^{-1}	6.09×10^{-8}	1.00×10^{-6}	3.79×10^{-14}	1.76×10^{-1}	9.20×10^{-10}	3.95×10^{-10}
0.5	4.00×10^{-7}	7.36×10^{-1}	1.05×10^{-6}	2.22×10^{-5}	6.86×10^{-13}	4.13×10^{-1}	3.44×10^{-8}	6.27×10^{-9}
0.1	9.98×10^{-6}	9.39×10^{-1}	3.51×10^{-4}	6.64×10^{-3}	4.63×10^{-10}	8.48×10^{-1}	5.12×10^{-5}	3.68×10^{-6}
0.05	3.99×10^{-5}	9.69×10^{-1}	2.72×10^{-3}	3.54×10^{-2}	7.17×10^{-9}	9.22×10^{-1}	6.37×10^{-4}	5.45×10^{-5}
0.01	9.83×10^{-4}	9.94×10^{-1}	8.81×10^{-2}	3.55×10^{-1}	3.22×10^{-6}	9.84×10^{-1}	4.32×10^{-2}	1.82×10^{-2}
0.005	3.86×10^{-3}	9.97×10^{-1}	2.27×10^{-1}	5.68×10^{-1}	3.62×10^{-5}	9.92×10^{-1}	1.36×10^{-1}	1.27×10^{-1}
0.001	7.95×10^{-2}	9.99×10^{-1}	6.90×10^{-1}	8.84×10^{-1}	4.15×10^{-3}	9.98×10^{-1}	5.76×10^{-1}	7.48×10^{-1}

Complexometric EDTA Titration Curves
     Now that we know something about EDTA's chemical properties, we are ready to evaluate its utility as a titrant for the analysis of metal ions. To do so we need to know the shape of a complexometric EDTA titration curve. We saw that an acid-base titration curve shows the change in pH following the addition of titrant. The analogous result for a titration with EDTA shows the change in pM, where M is the metal ion, as a function of the volume of EDTA.

Calculating the Titration Curve
     As an example, let's calculate the titration curve for 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA at a pH of 10 and in the presence of 0.0100 M NH_3. The formation constant for Cd^{2+}- EDTA is 2.9×10^{16}.
     Since the titration is carried out at a pH of 10, some of the EDTA is present in forms other than Y^{4-}. In addition, the presence of NH_3 means that the EDTA must compete for the Cd_{2+}. To evaluate the titration curve, therefore, we must use the appropriate conditional formation constant. We find that $\alpha_{Y^{4-}}$ is 0.35 at a pH of 10, and that $\alpha_{cd^{2+}}$ is
0.0881 when the concentration of NH_3 is 0.0100 M. Using these values, we calculate that the conditional formation constant is

$K_f" = \alpha_{cd^{2+}}$ X $\alpha_{Y^{4-}}$ x $K_f = (0.35)(0.0881)(2.9 \times 10^{16}) = 8.9 \times 10^{14}$

Because $K_f"$ is so large, we treat the titration reaction as though it proceeds to completion.

      The first task in calculating the titration curve is to determine the volume of EDTA needed to reach the equivalence point. At the equivalence point we know that

$$\text{Moles EDTA = Moles Cd}^{2+}$$

or

$$M_{EDTA}V_{EDTA} = M_{Cd}V_{Cd}$$

Solving for the volume of EDTA

$$V_{EDTA} = \frac{M_{Cd}V_{Cd}}{M_{EDTA}} = \frac{(0.005\ M)(50.0\ mL)}{(0.01\ M)} = 25.0\ mL$$

shows us that 25.0 mL of EDTA is needed to reach the equivalence point.

      Before the equivalence point, Cd^{2+} is in excess, and pCd is determined by the concentration of free Cd^{2+} remaining in solution. Not all the untitrated Cd$_{2+}$ is free (some is complexed with NH$_3$), so we will have to account for the presence of NH$_3$.

      For example, after adding 5.0 mL of EDTA, the total concentration of Cd^{2+} is

$$C_{Cd} = \frac{\text{moles excess Cd}^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd} - M_{EDTA}V_{EDTA}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(0.005\ M)(50.0\ mL) - (0.010\ M)(5.0\ mL)}{50.0\ mL + 5.0\ mL} = 3.64 \times 10^{-3}\ M$$

To calculate the concentration of free Cd^{2+} we use equation

$$\alpha_{cd^{2+}} = \frac{[Cd^{2+}]}{C_{cd}}$$

$[Cd^{2+}] = \alpha_{cd^{2+}}$ x $C_{cd} = (0.0881)(3.64 \times 10^{-3}\ M) = 3.21 \times 10^{-4}\ M$
Thus, pCd is

$pCd = -\log[Cd^{2+}] = -\log(3.21 \times 10^{-4}) = 3.49$

At the equivalence point, all the Cd^{2+} initially present is now present as CdY^{2-}. The concentration of Cd^{2+}, therefore, is determined by the dissociation of the CdY^{2-} complex. To find pCd we must first calculate the concentration of the complex.

$$[CdY^{2-}] = \frac{\text{initial moles } Cd^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(0.005 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 25.0 \text{ mL}} = 3.33 \times 10^{-3} \text{ M}$$

Letting the variable x represent the concentration of Cd^{2+} due to the dissociation of the CdY^{2-} complex, we have

$$K_f{}'' = \frac{[CdY^{2-}]}{C_{cd} \, C_{EDTA}} = \frac{3.33 \times 10^{-3}}{(X)(X)} = 8.94 \times 10^{14}$$

$X = C_{Cd} = 1.93 \times 10^{-9} \text{ M}$
Once again, to find the $[Cd^{2+}]$ we must account for the presence of NH_3; thus
$[Cd^{2+}] = \alpha_{cd^{2+}} \times C_{cd} = (0.0881)(1.93 \times 10^{-9} \text{ M}) = 1.70 \times 10^{-10} \text{ M}$
giving pCd as 9.77.

After the equivalence point, EDTA is in excess, and the concentration of Cd^{2+} is determined by the dissociation of the CdY^{2-} complex. Examining the equation for the complex's conditional formation constant, we see that to calculate C_{Cd} we must first calculate $[CdY^{2-}]$ and C_{EDTA}. After adding 30.0 mL of EDTA, these concentrations are

$$[CdY^{2-}] = \frac{\text{initial moles } Cd^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(0.005 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 30.0 \text{ mL}} = 3.13 \times 10^{-3} \text{ M}$$

$$C_{EDTA} = \frac{\text{moles excess EDTA}}{\text{total volume}} = \frac{M_{EDTA}V_{EDTA} - M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(0.01 \text{ M})(30.0 \text{ mL}) - (0.005 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 30.0 \text{ mL}} = 6.25 \times 10^{-4} \text{ M}$$

Substituting these concentrations into equation

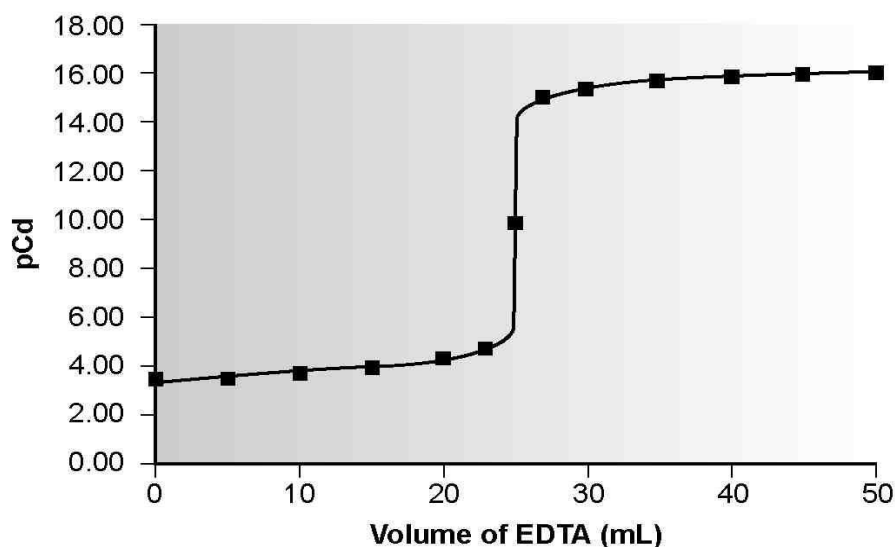$$K_f'' = \frac{[CdY^{2-}]}{C_{cd} \, C_{EDTA}}$$

and solving for C_{Cd} gives

$$K_f'' = \frac{[CdY^{2-}]}{C_{cd} \, C_{EDTA}} = \frac{3.13 \times 10^{-3} \text{ M}}{C_{cd} \, (6.25 \times 10^{-4} \text{ M})} = 8.94 \times 10^{14}$$

$C_{Cd} = 5.6 \times 10^{-15}$ M

Thus,

$$[Cd^{2+}] = \alpha cd^{2+} \times C_{cd} = (0.0881)(5.6 \times 10^{-15} \text{ M}) = 4.93 \times 10^{-16} \text{ M}$$

and pCd is 15.31.

Complexometric titration curve for 50.0 mL of 5.00 x 10^{-3} M Cd$_{2+}$with 0.0100 M EDTA at a pH of 10.0 in the presence of 0.0100 M NH$_3$.

Volume of EDTA (mL)	pCd
0.00	3.36
5.00	3.49
10.00	3.66
15.00	3.87
20.00	4.20
23.00	4.62
25.00	9.77
27.00	14.91
30.00	15.31
35.00	15.61
40.00	15.78
45.00	15.91
50.00	16.01

Data for Titration of 5.00 x 10$_3$ M Cd^{2+} with 0.0100 M EDTA at a pH of 10.0 and in the Presence of 0.0100 M NH$_3$

Methods for finding the end point in Precipitation Titration

1- Finding the End Point with a Visual Indicator.
     Most indicators for complexation titrations are organic dyes that form stable complexes with metal ions. These dyes are known as **metallochromic indicators.**
2- Finding the End Point by Monitoring Absorbance.

References

- Modern of analytical chemistry by David Harvey (DePauw University).
- Fundamental of Analytical Chemistry,8th Edition,Skoog.