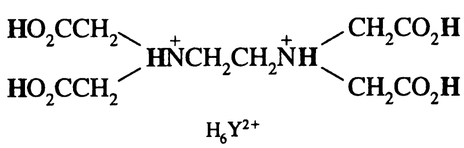
Chem 321 Lecture 25 - Complexometric Titrations
12/3/13

Student Learning Objectives

EDTA

After the Co^{2+} in your unknown is separated from Fe^{3+} it can be quantitatively measured by a **complexometric titration**. In such a titration, a metal ion is titrated with a ligand that readily forms a complex with the metal ion. Ethylenediaminetetraacetic acid (**EDTA**) is used to complex the Co^{2+}. EDTA is a **polydentate ligand**. This means that it can donate more than one pair of nonbonding electrons when forming a complex with a metal ion. In fact, EDTA can form 6 bonds with a metal ion and thus occupy all the octahedral positions associated with a metal ion complex. The structure of the fully protonated form of EDTA (H_6Y^{2+}) is shown in Figure 18.1.



$pK_1 = 0.0$
$pK_2 = 1.5$
$pK_3 = 2.0$
$pK_4 = 2.66$
$pK_5 = 6.16$
$pK_6 = 10.24$

Figure 18.1 Structure of fully protonated EDTA

EDTA can lose the six highlighted hydrogens when it complexes with a metal ion. The nonbonding electron pairs on the nitrogen and on oxygen in the four carboxyl groups are used to form the metal ion - EDTA complex. Notice that as in ethylenediamine and phenanthroline there is a 2-carbon bridge between adjacent electrons pairs used by EDTA for complexing metal ions.

The fully ionized form of EDTA (Y^{4-}) will form a 1:1 complex with virtually all metal ions in solution. The formation of this complex can be represented by

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$$

with an equilibrium constant (K_f) given by

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

The values of log K_f for various metal ions are given in the table below. Notice that K_f is often quite large, especially for highly-charged metal ions.

TABLE 11-2 Formation constants for metal-EDTA complexes

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.95	V^{3+}	25.9[a]	Tl^{3+}	35.3
Na^+	1.86	Cr^{3+}	23.4[a]	Bi^{3+}	27.8[a]
K^+	0.8	Mn^{3+}	25.2	Ce^{3+}	15.93
Be^{2+}	9.7	Fe^{3+}	25.1	Pr^{3+}	16.30
Mg^{2+}	8.79	Co^{3+}	41.4	Nd^{3+}	16.51
Ca^{2+}	10.65	Zr^{4+}	29.3	Pm^{3+}	16.9
Sr^{2+}	8.72	Hf^{4+}	29.5	Sm^{3+}	17.06
Ba^{2+}	7.88	VO^{2+}	18.7	Eu^{3+}	17.25
Ra^{2+}	7.4	VO_2^+	15.5	Gd^{3+}	17.35
Sc^{3+}	23.1[a]	Ag^+	7.20	Tb^{3+}	17.87
Y^{3+}	18.08	Tl^+	6.41	Dy^{3+}	18.30
La^{3+}	15.36	Pd^{2+}	25.6[a]	Ho^{3+}	18.56
V^{2+}	12.7[a]	Zn^{2+}	16.5	Er^{3+}	18.89
Cr^{2+}	13.6[a]	Cd^{2+}	16.5	Tm^{3+}	19.32
Mn^{2+}	13.89	Hg^{2+}	21.5	Yb^{3+}	19.49
Fe^{2+}	14.30	Sn^{2+}	18.3[b]	Lu^{3+}	19.74
Co^{2+}	16.45	Pb^{2+}	18.0	Th^{4+}	23.2
Ni^{2+}	18.4	Al^{3+}	16.4	U^{4+}	25.7
Cu^{2+}	18.78	Ga^{3+}	21.7		
Ti^{3+}	21.3	In^{3+}	24.9		

NOTE: The stability constant is the equilibrium constant for the reaction $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$. Values in table apply at 25°C and ionic strength 0.1 M unless otherwise indicated.

a. 20°C, ionic strength = 0.1 M. b. 20°C, ionic strength = 1 M.

SOURCE: A. E. Martell, R. M. Smith, and R. J. Motekaitis, NIST Critically Selected Stability Constants of Metal Complexes, NIST Standard Reference Database 46, Gaithersburg, MD, 2001.

Harris, *Quantitative Chemical Analysis*, 8e

K_f is greater than 10^{16} for the formation of the EDTA-Co^{2+} complex. This makes for a quantitative titration reaction, however, it assumes that all of the EDTA is in the fully ionized form. For any polyprotic acid like EDTA, the amount of any particular ionized form (such as Y^{4-}) depends on the solution pH. The fraction of EDTA that is in the Y^{4-} form (α_{Y4-}) is given by

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

where [EDTA] is the total concentration of uncomplexed EDTA in solution. This fraction can be calculated for a given pH from the K_a values for the polyprotic EDTA. The values of α_{Y4-} in the table below indicate that, as expected, only in very basic solution (pH>12) is the EDTA fully ionized. However, it is difficult to titrate metal ions in basic solution because of competing reactions such as the formation of metal hydroxides.

TABLE 11-1 Values of $\alpha_{Y^{4-}}$ for EDTA at 25°C and μ = 0.10 M

pH	$\alpha_{Y^{4-}}$
0	1.3×10^{-23}
1	1.4×10^{-18}
2	2.6×10^{-14}
3	2.1×10^{-11}
4	3.0×10^{-9}
5	2.9×10^{-7}
6	1.8×10^{-5}
7	3.8×10^{-4}
8	4.2×10^{-3}
9	0.041
10	0.30
11	0.81
12	0.98
13	1.00
14	1.00

Harris, *Quantitative Chemical Analysis*, 8e

To account for the effect of pH on the ionization of the EDTA, it is convenient to rewrite the equilibrium expression for the complex formation as

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

and to define a conditional formation constant (K_f') which is given by

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

The value of K_f' provides information about how quantitative the complex formation is at a given pH. Since α_{Y4-} is very small at acidic pH values, there is generally some minimum pH for which the complex formation reaction is sufficiently quantitative. Using an arbitrarily chosen value of $K_f' = 10^6$ for an effective titration, a plot of the minimum pH to achieve this for various metal ions is given in Figure 18.2. For Co^{2+}, this corresponds to a pH greater than 4. In our experiment, the titration solution is buffered at a pH = 5.8 to ensure a quantitative reaction between Co^{2+} and EDTA. It is useful to note that the fully ionized form of EDTA (Y^{4-}) is not the only form of EDTA that reacts with metal ions.

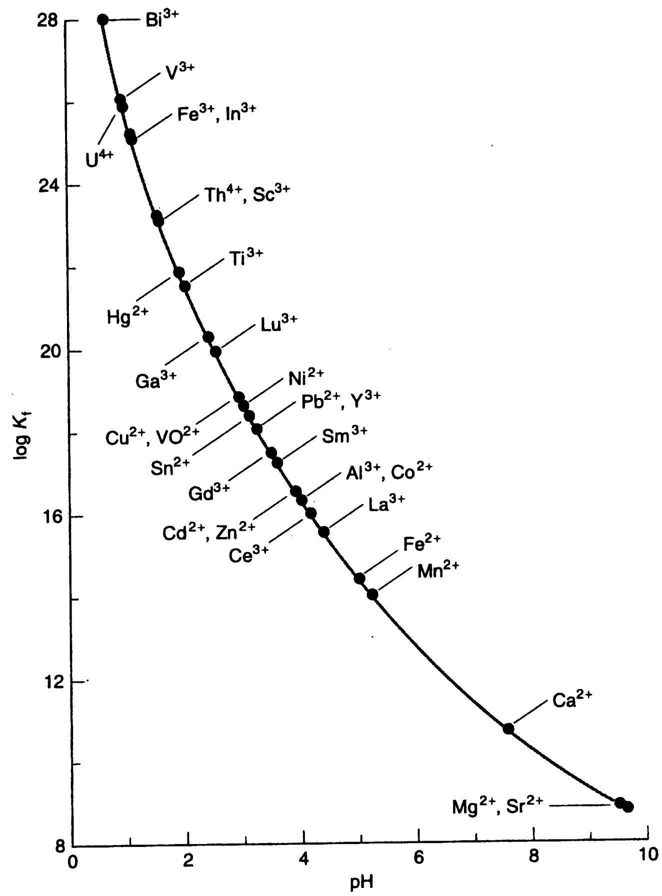
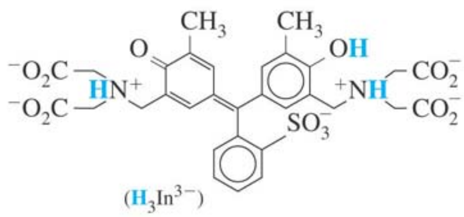


Figure 18.2 Minimum pH needed for a conditional formation constant of 10^6

The particular pH used to buffer the titration solution was also chosen because of the **metal ion indicator** used to signal the end point in the titration. A metal ion indicator is a substance that changes color when it binds to metal ions in solution. Metal ion indicators tend to be polyprotic complexing agents. Xylenol orange (Fig. 18.3) is used for the cobalt titration. This indicator is red when it forms a complex with metal ions such as Co^{2+}. However, the color of the unbound (free) indicator depends on pH and which protonated form is predominantly present (Fig. 18.3). Above pH = 6.7, free xylenol orange is violet and the color change from red to violet is not sharp. However, below pH = 6.7 the free indicator color is yellow and the change from red to yellow is much easier to see.

Xylenol orange



$pK_2 = 2.32$
$pK_3 = 2.85$
$pK_4 = 6.70$
$pK_5 = 10.47$
$pK_6 = 12.23$

H_5In^-	yellow
H_4In^{2-}	yellow
H_3In^{3-}	yellow
H_2In^{4-}	violet
HIn^{5-}	violet
In^{6-}	violet

Figure 18.3 Structure of the metal ion indicator xylenol orange

A small amount of xylenol orange is added initially to the cobalt solution and it forms a complex with some of the Co^{2+}. As EDTA is added to this solution, the EDTA complexes the free Co^{2+}. Just before the equivalence point, the free Co^{2+} is used up and the EDTA starts to remove cobalt ion from the indicator. As the xylenol orange loses the metal ion, its color changes. Obviously, the indicator must not bind the metal ion as strongly as the complexing agent (EDTA) used for the titration.

Check for Understanding 18.1 **Solutions**

1. What is the concentration of uncomplexed Co^{2+} in solution at the equivalence point in an EDTA titration if 25.00 mL of 0.0100 M EDTA solution is needed to titrate the sample? Assume the unknown solution volume is 75.00 mL and that it is buffered to a pH = 6.0.

2. How many ppth of the original Co^{2+} in the unknown solution does this uncomplexed cobalt represent?

Exercises for Complexometric Titrations