PHARMACEUTICAL ANALYTICAL CHEMISTRY

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Complexometric Titrations

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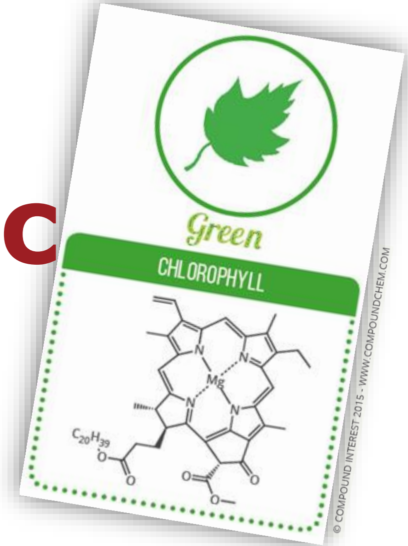
Complexometric Titrations

Chapter 9



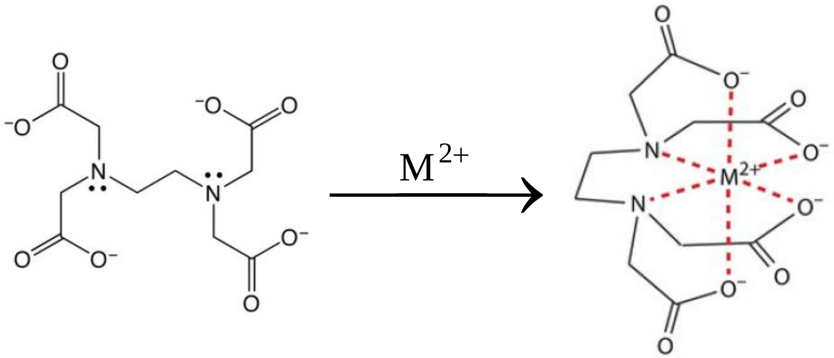
Learning Objectives

- *To calculate formation constants for EDTA equilibrium*
- *To explain the principles of indicators used in complexometric titrations*
- *To disctibe the effect of pH on the stability of complexes*
- *To calculate titration curve for complexometric titrations*
- *To calculate the concentration of metal analytes using EDTA volumetric methods*

Complexometric Titrations

Key Concepts

- The technique involves titrating metal ions with a complexing agent or chelating agent (Ligand)
- Ligands (or complexing agents or chelating agents) can be any electron donating entity, which has the ability to bind to the metal ion and produce a complex ion, Ex: H_2O, NH_3, Cl^-, Br^-, I^-…….
- Ethylenediaminetetraacetic acid (EDTA or H_4Y) is an aminocarboxylic acid. In its fully deprotonated form (Y^{4-}), it has six binding sites—four negatively charged carboxylate groups and two tertiary amino groups—that can donate six pairs of electrons to a metal ion. 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.

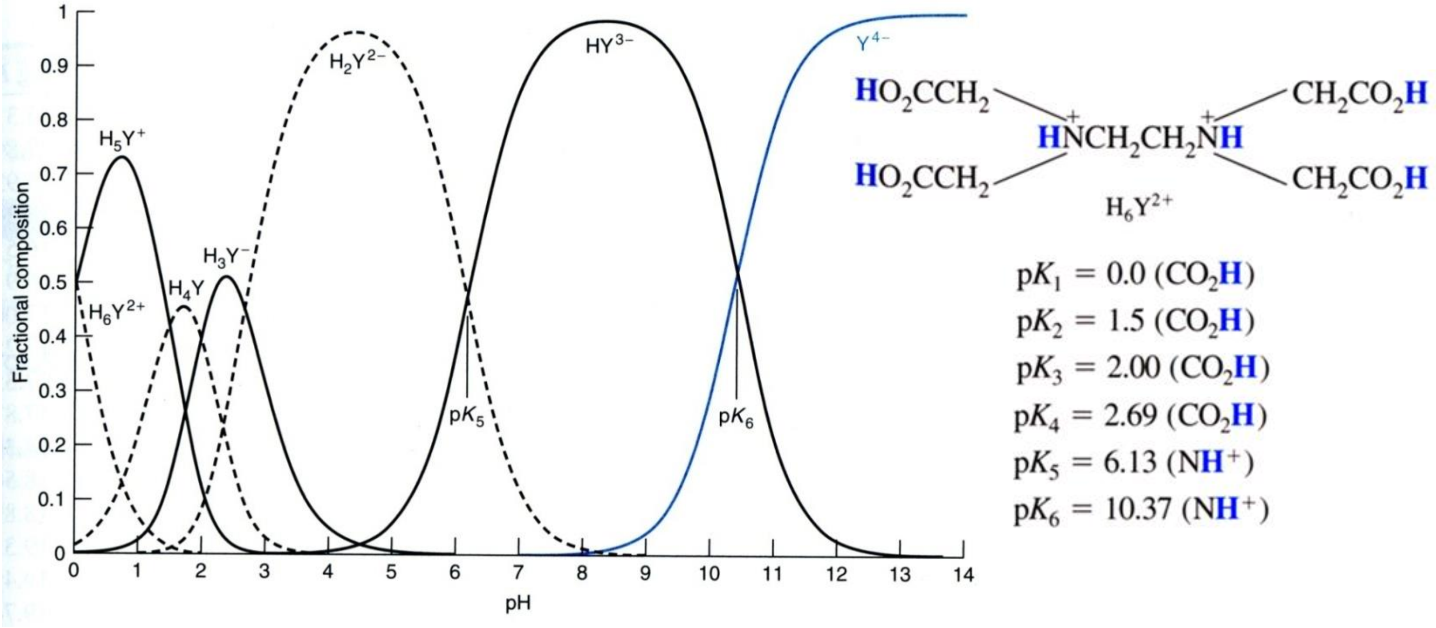


Complexometric Titrations

Factors influencing EDTA reactions:

- The nature and activity of metal ion.
- The pH at which the titration is carried out.
- The presence of interfering ions such as CN^-, Citrate, Tartrate, F^- and other complex forming agents.
- Organic solvents also increase the stability of complex.

Effect of pH:



$pK_1 = 0.0\ (CO_2H)$

$pK_2 = 1.5\ (CO_2H)$

$pK_3 = 2.00\ (CO_2H)$

$pK_4 = 2.69\ (CO_2H)$

$pK_5 = 6.13\ (NH^+)$

$pK_6 = 10.37\ (NH^+)$

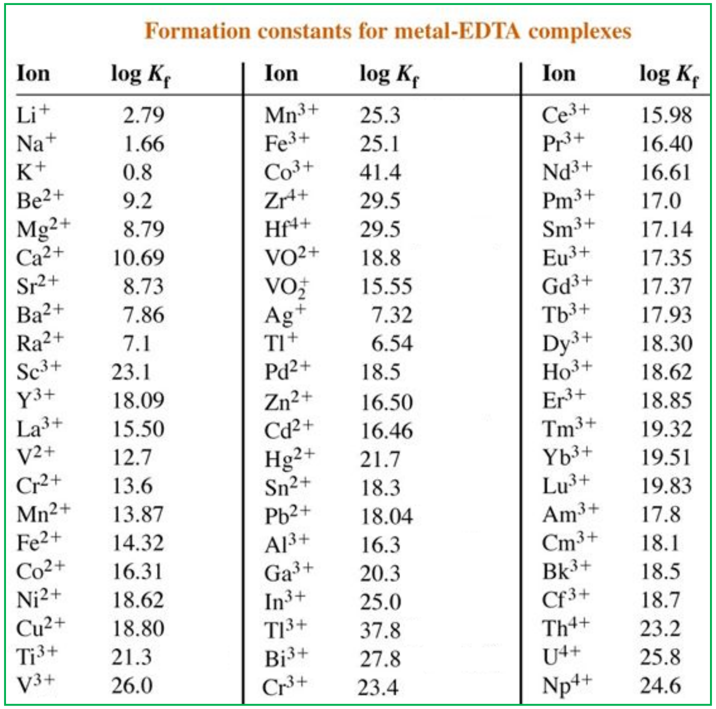
EDTA Titrations

- The basic form of EDTA (Y^{4-}) reacts with most metal ions to form a 1:1 complex.

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

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

- Fraction (α) of the most basic form of EDTA (Y^{4-}) is defined by the H^+ concentration and acid-base equilibrium constants



Formation constants for metal-EDTA complexes

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.79	Mn^{3+}	25.3	Ce^{3+}	15.98
Na^+	1.66	Fe^{3+}	25.1	Pr^{3+}	16.40
K^+	0.8	Co^{3+}	41.4	Nd^{3+}	16.61
Be^{2+}	9.2	Zr^{4+}	29.5	Pm^{3+}	17.0
Mg^{2+}	8.79	Hf^{4+}	29.5	Sm^{3+}	17.14
Ca^{2+}	10.69	VO^{2+}	18.8	Eu^{3+}	17.35
Sr^{2+}	8.73	VO_2^+	15.55	Gd^{3+}	17.37
Ba^{2+}	7.86	Ag^+	7.32	Tb^{3+}	17.93
Ra^{2+}	7.1	Tl^+	6.54	Dy^{3+}	18.30
Sc^{3+}	23.1	Pd^{2+}	18.5	Ho^{3+}	18.62
Y^{3+}	18.09	Zn^{2+}	16.50	Er^{3+}	18.85
La^{3+}	15.50	Cd^{2+}	16.46	Tm^{3+}	19.32
V^{2+}	12.7	Hg^{2+}	21.7	Yb^{3+}	19.51
Cr^{2+}	13.6	Sn^{2+}	18.3	Lu^{3+}	19.83
Mn^{2+}	13.87	Pb^{2+}	18.04	Am^{3+}	17.8
Fe^{2+}	14.32	Al^{3+}	16.3	Cm^{3+}	18.1
Co^{2+}	16.31	Ga^{3+}	20.3	Bk^{3+}	18.5
Ni^{2+}	18.62	In^{3+}	25.0	Cf^{3+}	18.7
Cu^{2+}	18.80	Tl^{3+}	37.8	Th^{4+}	23.2
Ti^{3+}	21.3	Bi^{3+}	27.8	U^{4+}	25.8
V^{3+}	26.0	Cr^{3+}	23.4	Np^{4+}	24.6

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

where [EDTA] is the total concentration of all free EDTA species in solution

α_{Y4-} *is depended on the pH of the solution*

$$\alpha_{Y^{4-}} = \frac{K_1K_2K_3K_4K_5K_6}{\{[H^+]^6 + [H^+]^5K_1 + [H^+]^4K_1K_2 + [H^+]^3K_1K_2K_3 + [H^+]^2K_1K_2K_3K_4 + [H^+]K_1K_2K_3K_4K_5 + K_1K_2K_3K_4K_5K_6\}}$$

EDTA Titrations

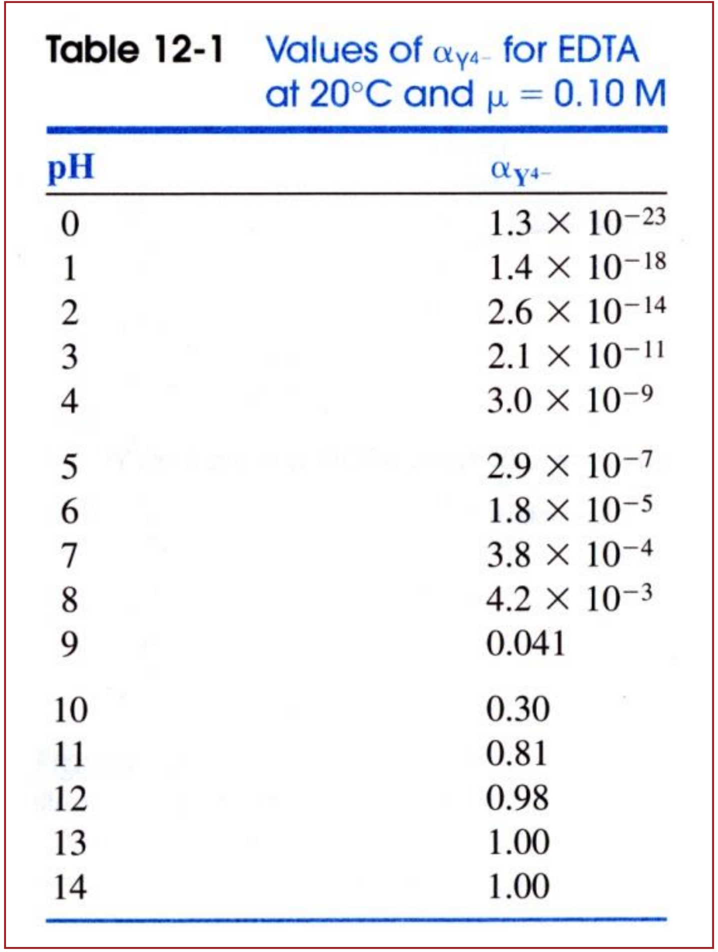


Table 12-1 Values of $\alpha_{Y^{4-}}$ for EDTA at 20°C and $\mu = 0.10$ M

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

The concentration of Y^{4-} and the total concentration of EDTA is solution [EDTA] are related as follows:

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

⇨ The formation constant will be

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

at fixed pH **conditional formation constant (K'_f)** could be calculated as following

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

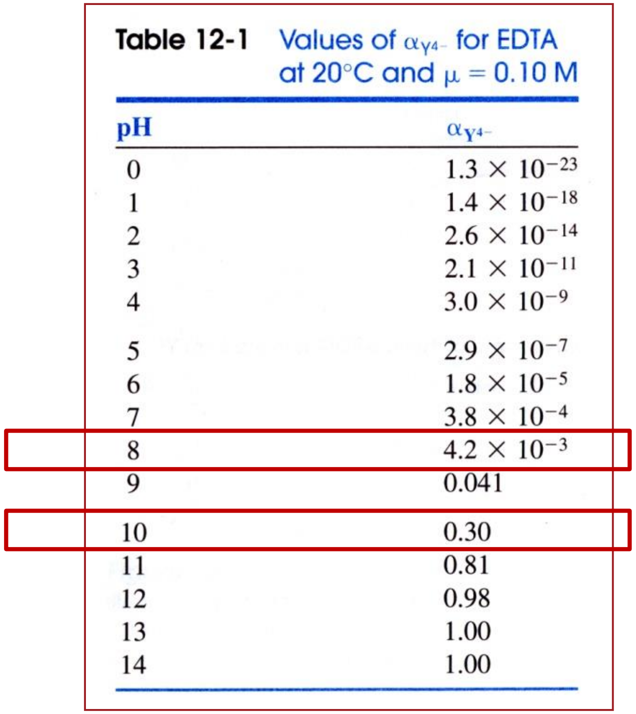
EDTA Titrations

Example:

Calculate the molar Y^{4-} concentration in a 0.0200M EDTA solution buffered to a pH of 10.00

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

$$= 0.3 \text{ x } 0.0200 = 0.0060\text{M}$$



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Example

Calculate the equilibrium concentration of Ni^{2+} in a solution with an analytical NiY^{2-} concentration of 0.0150M at pH 8.0 ($K_f = 4.2\text{x}10^{18}$) .

$$\begin{array}{ccccc} NiY^{2-} & \rightleftharpoons & Ni^{2+} & + & \overbrace{(Y^{4-} + HY^{3-} + H_2Y^{2-} + H_3Y^{-} + H_4Y)}^{EDTA} \\ 0.015\text{-x} & & \text{x} & & \text{x} \end{array}$$

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

$K'_f = 4.2\text{x}10^{18} \text{ x } 4.2\text{x}10^{-3} = 1.76\text{x}10^{15} = 0.015/x^2$

$x = [Ni^{2+}] = \sqrt{(0.015/1.76\text{x}10^{15})} = 2.9\text{x}10^{-9}\text{M}$

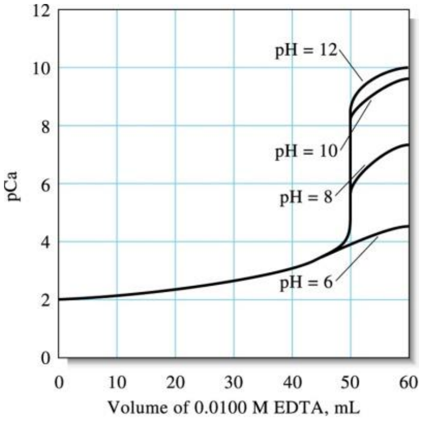
EDTA Titrations

Question:

What is the concentration of free Fe^{3+} in a solution of 0.10 M FeY^{-} at (a) pH 2.0, (b) pH 8.0? ($K_f = 1.3 \times 10^{25}$, $\alpha_{Y^{4-}(pH\ 2)} = 2.6 \times 10^{-14}$, $\alpha_{Y^{4-}(pH\ 8)} = 4.2 \times 10^{-3}$).

Answer: $[Fe^{3+}] = 5.4 \times 10^{-7}$ at pH 2.0 and $[Fe^{3+}] = 1.4 \times 10^{-12}$ at pH 8.0

- Note that the metal –EDTA complex becomes less stable as pH decreases (K'_f decreases).
- In order to get a "complete" titration ($K'_f \geq 10^6$), EDTA requires a certain minimum pH for the titration of each metal ion.
- By adjusting the pH of an EDTA titration: metal ion (e.g. Fe^{3+}) can be titrated without interference from others (e.g. Ca^{2+})



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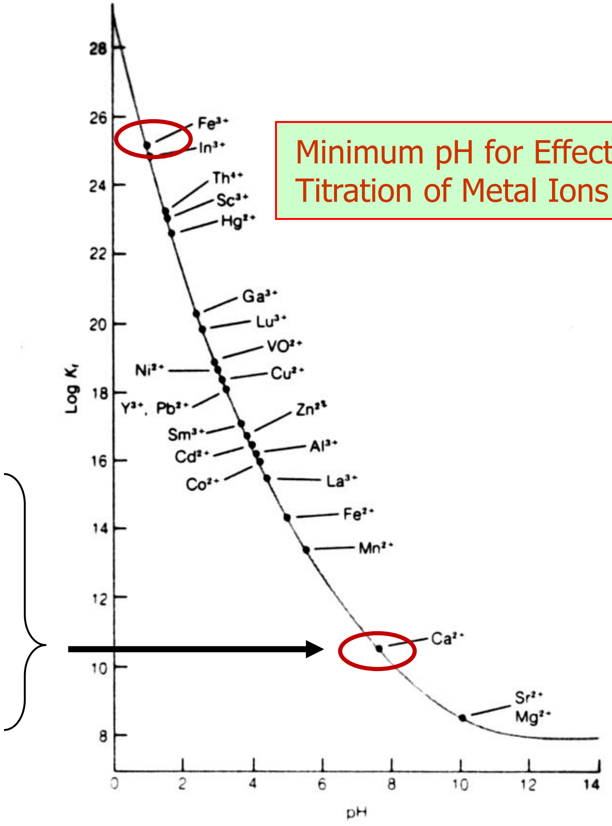


Minimum pH for Effective Titration of Metal Ions

Complexometric EDTA Titration Curves

- **Complexation titration curve shows the change in pM, where M is the metal ion, as a function of the volume of EDTA.**

- **Calculating the Titration Curve**

  Step 1: Calculate the conditional formation constant for the metal–EDTA complex.

  Step 2: Calculate the volume of EDTA needed to reach the equivalence point.

  Step 3: Calculate pM values before the equivalence point by determining the concentration of **remaining unreacted metal ions**.

  Step 4: Calculate pM at the equivalence point **using the conditional formation constant and Complex concentration**.

  Step 5: Calculate pM after the equivalence point **using the conditional formation constant, excess concentration of EDTA and Complex concentration**.

Complexometric EDTA Titration Curves

Let's calculate the titration curve for 50.0 mL of 5.00×10^{-3} M Cd^{2+} using a titrant of 0.0100 M EDTA at pH 10.0 (assume K_f is $2.9\text{x}10^{15}$ and $\alpha_{Y^{4-}(pH\ 10)}$ is 0.3)

Step 1: Calculate the conditional formation constant for the metal–EDTA complex.

$$K'_f = K_f \text{ x } \alpha_{Y^{4-}} = 2.9\text{x}10^{15} \text{ x } 0.3 = 8.7\text{x}10^{14}$$

Step 2: Calculate the volume of EDTA needed to reach the equivalence point.

at the equivalence point

moles EDTA = moles Cd^{2+}

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

$$\Rightarrow V_{eq} = V_{EDTA} = M_{Cd}V_{Cd} / M_{EDTA}$$

$$= (5.00\times10^{-3}\text{ M})(50.0\text{ mL}) / (0.0100\text{ M}) = 25.0\text{ mL}$$

Complexometric EDTA Titration Curves

Step 3: Calculate pM values before the equivalence point by determining the concentration of unreacted metal ions.

Before the equivalence point, Cd^{2+} is present in excess and pCd is determined by the concentration of unreacted Cd^{2+}.

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

$$C_{Cd} = (\text{initial moles } Cd^{2+} - \text{moles EDTA added}) / \text{total volume}$$

$$= (M_{Cd}V_{Cd} - M_{EDTA}V_{EDTA}) / (V_{Cd} + V_{EDTA})$$

$$= ((5.00\times10^{-3}\text{ M})(50.0\text{ mL}) - (0.0100\text{ M})(5.0\text{ mL})) / (50.0\text{mL} + 5.0\text{mL})$$

$$= 3.64\times10^{-3}\text{ M}$$

$$pCd = -\text{Log}(3.64\times10^{-3}) = 2.44$$

Complexometric EDTA Titration Curves

Step 4: Calculate pM at the equivalence point using the conditional formation constant.

at equivalence point all Cd^{2+} and EDTA converted to CdY^{2-},

$[CdY^{2-}]$ = initial moles Cd^{2+} / total volume = $M_{Cd}V_{Cd} / (V_{Cd} + V_{EDTA})$

$= (5.00\times10^{-3}\text{ M})(50.0\text{ mL}) / (50.0\text{ mL} + 25.0\text{ mL}) = 3.33\times10^{-3}\text{ M}$

(volume of equivalence was calculated and found to be 25.0 mL)

Now calculate C_{cd}

$$CdY^{2-} \rightleftharpoons Cd^{2+} + Y^{4-}$$

$$3.33\times10^{-3} - x \qquad x \qquad x$$

$K'_f = 8.7\text{x}10^{14} = [CdY^{-2}] / C_{Cd}C_{EDTA} = (3.33\times10^{-3} - x) / (x.x)$

⇨ $C_{Cd} = x = \sqrt{(3.33\times10^{-3} / 8.7\text{x}10^{14})} = 1.95\text{x}10^{-9}$

pCd = -Log($1.95\text{x}10^{-9}$)= 8.7

Complexometric EDTA Titration Curves

Step 5: Calculate pM after the equivalence point using the conditional formation constant:

At this stage CdY^{2-} formed and excess of EDTA present, their concentrations should be calculated. For example when 30.0 mL of EDTA added:

$[CdY^{2-}]$ = initial moles Cd^{2+} / total volume = $M_{Cd}V_{Cd} / (V_{Cd} + V_{EDTA})$

$= (5.00\times10^{-3}\ M)(50.0\ mL) / (50.0\ mL + 30.0\ mL) = 3.125\times10^{-3}\ M$

[EDTA] = (moles of EDTA added-initial moles Cd^{2+}) / total volume

$= M_{EDTA}V_{EDTA} - M_{Cd}V_{Cd} / (V_{Cd} + V_{EDTA})$

$= ((0.0100\ M)(30.0\ mL) - (5.00\times10^{-3}\ M)(50.0mL)) / (50.0\ mL + 30.0\ mL)$

$= 6.25\times10^{-4}\ M$

Now calculate C_{cd}

$$CdY^{2-} \rightleftharpoons Cd^{2+} + Y^{4-}$$

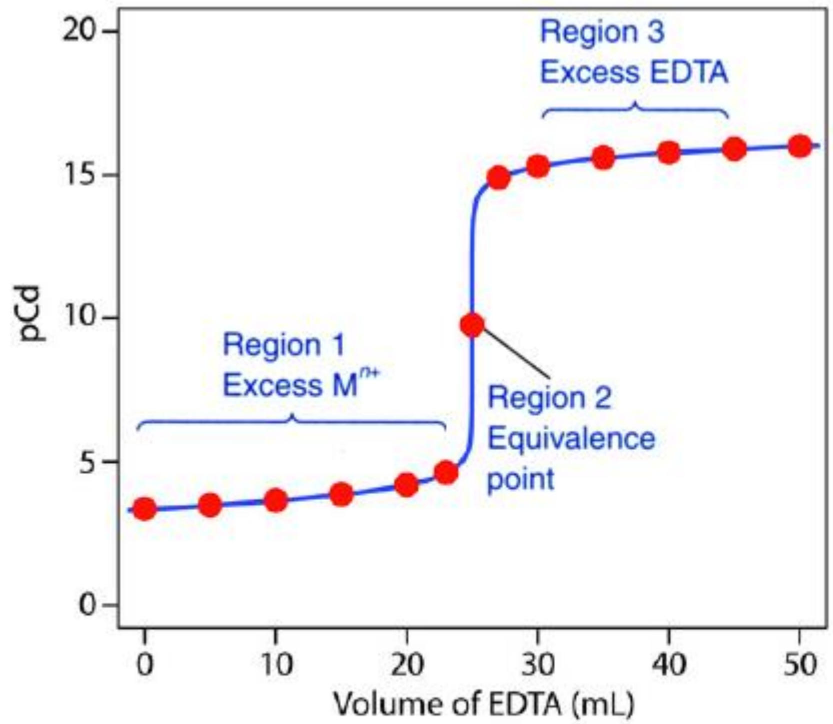
$$3.125\times10^{-3} - x \qquad x \qquad 6.25\times10^{-4} + x$$

$K'_f = 8.7x10^{14} = [CdY^{-2}] / C_{Cd}C_{EDTA} = (3.125\times10^{-3} - x) / (x)(6.25\times10^{-4} + x)$

⇨ $C_{Cd} = x = 3.125\times10^{-3} / (8.7x10^{14}\ x\ 6.25\times10^{-4}) = 5.75x10^{-15}$

pCd = $-Log(5.75x10^{-15}) = 14.2$

Complexometric EDTA Titration Curves

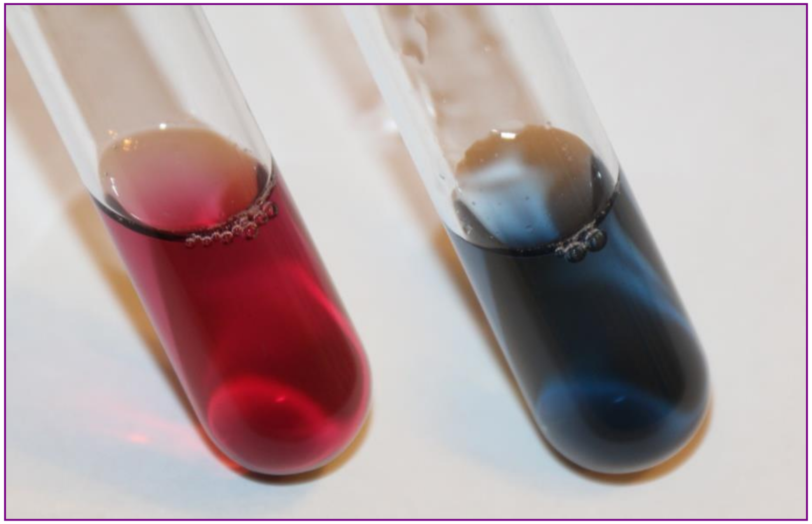


Determination Of EDTA Titration End Point

- Metal Ion Indicator: a compound that changes color when it binds to a metal ion
  - Similar to pH indicator, which changes color with pH or as the compound binds H^+
- For an EDTA titration, the indicator must bind the metal ion less strongly than EDTA
  - Needs to release metal ion to EDTA

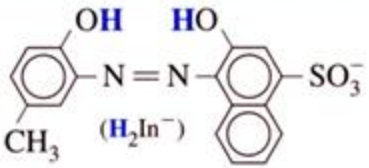
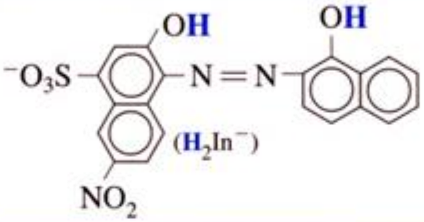
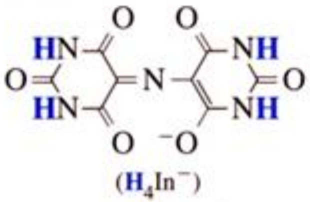
End Point indicated by a color change from red to blue

$$\underset{\text{(red)}}{\text{M–In}} + \underset{\text{(colorless)}}{\text{EDTA}} \longrightarrow \underset{\text{(colorless)}}{\text{M–EDTA}} + \underset{\text{(blue)}}{\text{In}}$$



Determination Of EDTA Titration End Point

- Common Metal Ion Indicators

Name	Structure	pK_a	Color of free indicator	Color of metal ion complex
Calmagite	 (H$_2$In$^-$)	pK_2 = 8.1 pK_3 = 12.4	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Eriochrome black T	 (H$_2$In$^-$)	pK_2 = 6.3 pK_3 = 11.6	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Murexide	 (H$_4$In$^-$)	pK_2 = 9.2 pK_3 = 10.9	H_4In^- red-violet H_3In^{2-} violet H_2In^{3-} blue	Yellow (with Co^{2+}, Ni^{2+}, Cu^{2+}); red with Ca^{2+}

Complexometric EDTA Titration

Example: The concentration of a solution of EDTA was determined by standardizing against a solution of Ca^{2+} prepared using a primary standard of $CaCO_3$. A 0.4071-g sample of $CaCO_3$ was transferred to a 500-mL volumetric flask, dissolved using a minimum of 6 M HCl, and diluted to volume. After transferring a 50.00-mL portion of this solution to a 250-mL Erlenmeyer flask, the pH was adjusted by adding 5 mL of a pH 10 NH_3/NH_4Cl buffer. After adding calmagite as an indicator, the solution was titrated with the EDTA, requiring 42.63 mL to reach the end point. Report the molar concentration of EDTA in the titrant. (M.wt. of $CaCO_3$ =100.09 g/mol)

Solution:

* The primary standard of Ca^{2+} has a concentration of

$$[0.4071 \text{ g } CaCO_3 / 100.09 \text{ g } CaCO_3] / (0.500 \text{ L}) = 8.135\times10^{-3} \text{ M } Ca^{2+}$$

* The moles of Ca^{2+} in the titrant is

$$8.135\times10^{-3} \text{ M } Ca^{2+} \times 0.050 \text{ L } Ca^{2+} = 4.068\times10^{-4} \text{ mol } Ca^{2+}$$

which means that 4.068×10^{-4} moles of EDTA are used in the titration.

* The molarity of EDTA in the titrant is

$$4.068\times10^{-4} \text{ mol EDTA} / 0.04263 \text{ L EDTA} = 9.543\times10^{-3} \text{ M EDTA}$$

References

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- YouTube https://www.youtube.com/watch?v=GfMveIZXq9A&list=PL9fwy3NUQKwbICh15S1cAUCJm1SxVhq19 أ.د. منذر عبداللطيف
- YouTube https://www.youtube.com/channel/UCh-WhopyMvQaMv0VF_h5O-Q/videos
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Thank You!