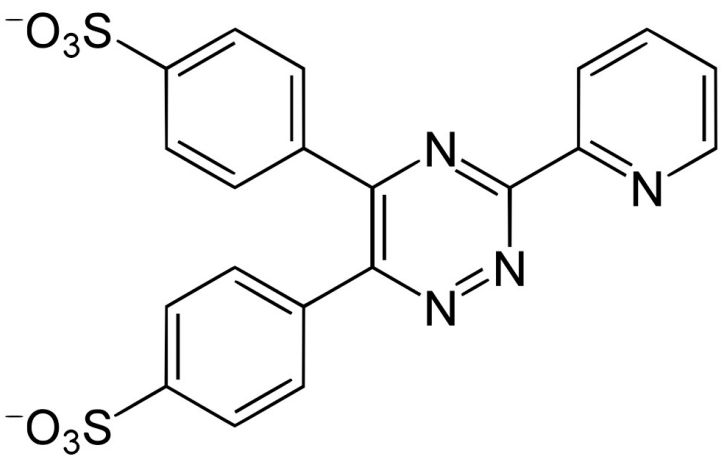
EDTA Titrations

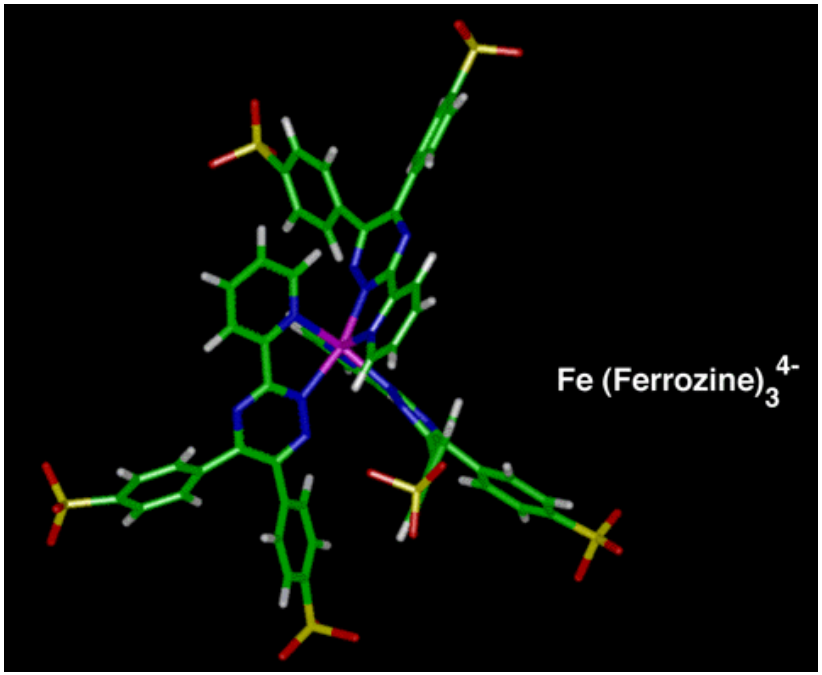
Chem M3LC
R. Corn

We already used metal complexation in Week 2 for the Fe Colorimetry Experiment:

$$Fe^{2+} + 3\ Fz^{2-} \Rightarrow Fe(Fz)_3^{4-}$$



Ferrozine (Fz^{2-})
is a metal ligand



Three Ferrozine will form a metal-ligand complex with Fe^{2+}

Metal Complex Formation Constants

Weak Metal Complex Formation Constants have similar values of K_1 to K_n

Zinc Complexation

1. Zinc-ammonia complexation

$Zn^{2+} + NH_3 = Zn(NH_3)^{2+}$	$K_1 = 180$	$\beta_1 = K_1 = 180$
$Zn(NH_3)^{2+} + NH_3 = Zn(NH_3)_2^{2+}$	$K_2 = 220$	$\beta_2 = K_1K_2 = 3.96 \times 10^4$
$Zn(NH_3)_2^{2+} + NH_3 = Zn(NH_3)_3^{2+}$	$K_3 = 250$	$\beta_3 = K_1K_2K_3 = 9.90 \times 10^6$
$Zn(NH_3)_3^{2+} + NH_3 = Zn(NH_3)_4^{2+}$	$K_4 = 110$	$\beta_4 = K_1K_2K_3K_4 = 1.09 \times 10^9$

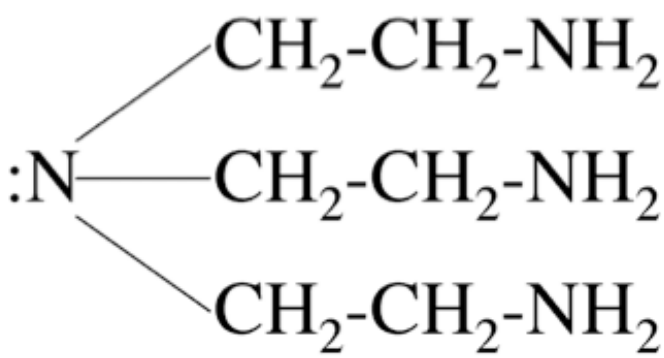
$$\alpha_{Zn^{2+}} = \frac{1}{1 + K_1[NH_3] + K_1K_2[NH_3]^2 + K_1K_2K_3[NH_3]^3 + K_1K_2K_3K_4[NH_3]^4}$$

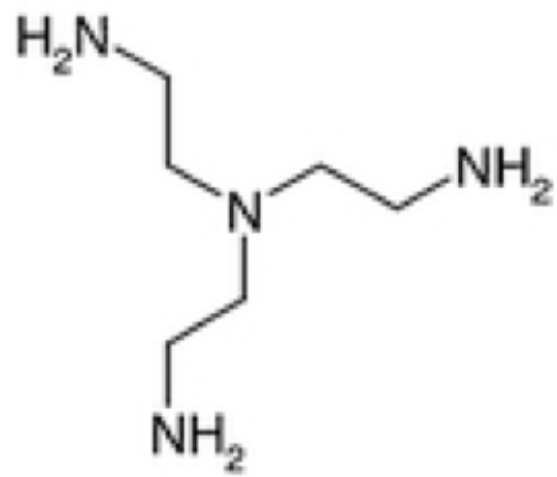
Therefore, many species co-exist in solution!

2. Zinc-tren complexation

$Zn^{2+} + tren = Zn(tren)^{2+}$ $\qquad$ $K_f = \beta_1 = 4.5 \times 10^{14}$

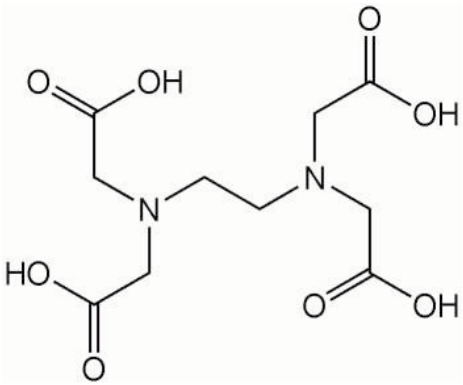
tren = triaminotriethylamine





$$\alpha_{Zn^{2+}} = \frac{1}{1 + K_f[tren]}$$

EDTA Metal Ion Complexation Equilibria



Ethylene Diamine Tetra-acetic Acid (H_4Y)

EDTA - the world's best metal ion chelator

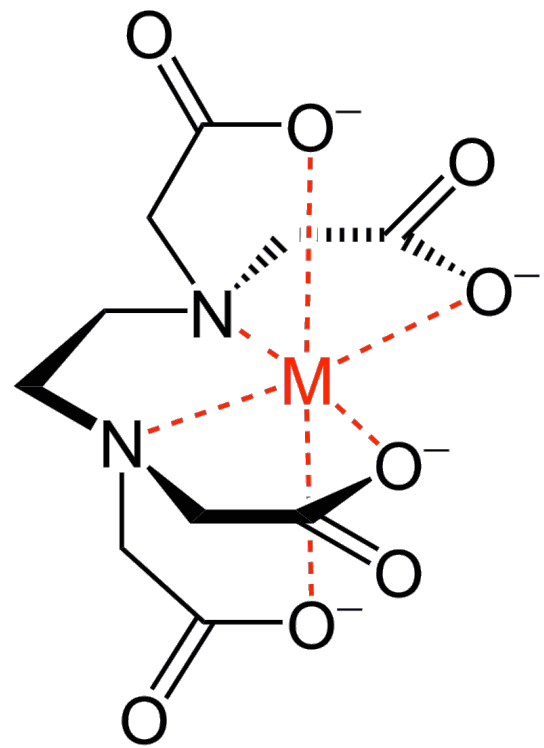
Metal complexation reactions with Y^{4-}:

$M^{n+} + Y^{4-} \rightarrow MnY^{(n-4)}$ $\quad K_f$

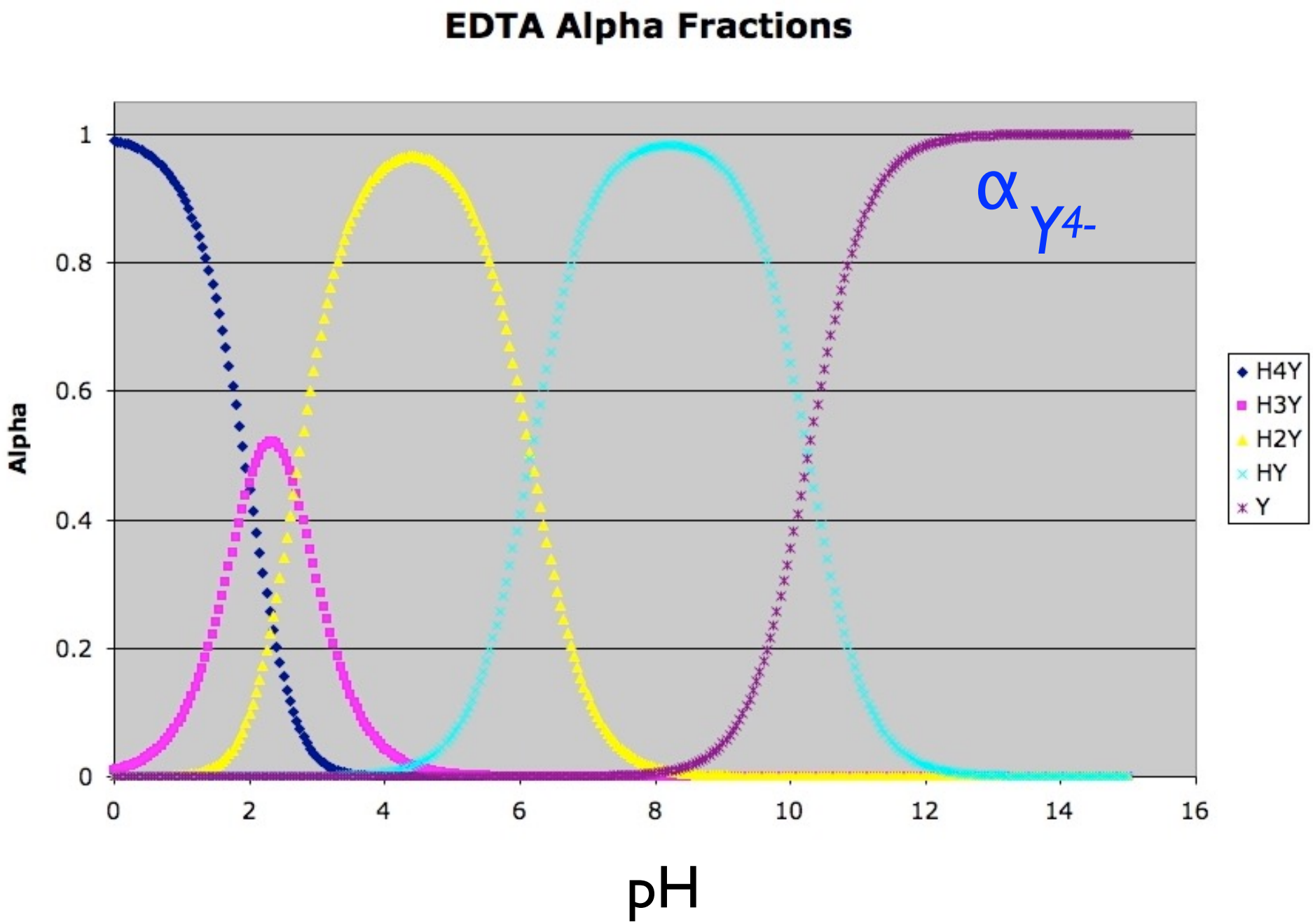
Metal Ion	log K_f
Ag^{+}	7.32
Mg^{2+}	8.69
Ca^{2+}	10.70
Co^{2+}	16.31
Cd^{2+}	16.46
Al^{3+}	15.89
Fe^{3+}	25.10
V^{3+}	25.90

Conditional formation constant: $K'_f = \alpha_{Y4-} K_f$

Y^{4-}



"Chelate"



Most EDTA titrations are performed at pH >= 10.

EDTA-Metal ion Complexation.

EDTA is a polyprotic acid - Ethylenediaminetetraacetic Acid. H_4Y.

$pK_1 = 1.99$; $pK_2 = 2.67$; $pK_3 = 6.16$; $pK_4 = 10.26$.

Alpha fraction for Y^{4-}:

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

$\alpha_{Y^{4-}}$ is equal to 0.35 at a pH of 10.

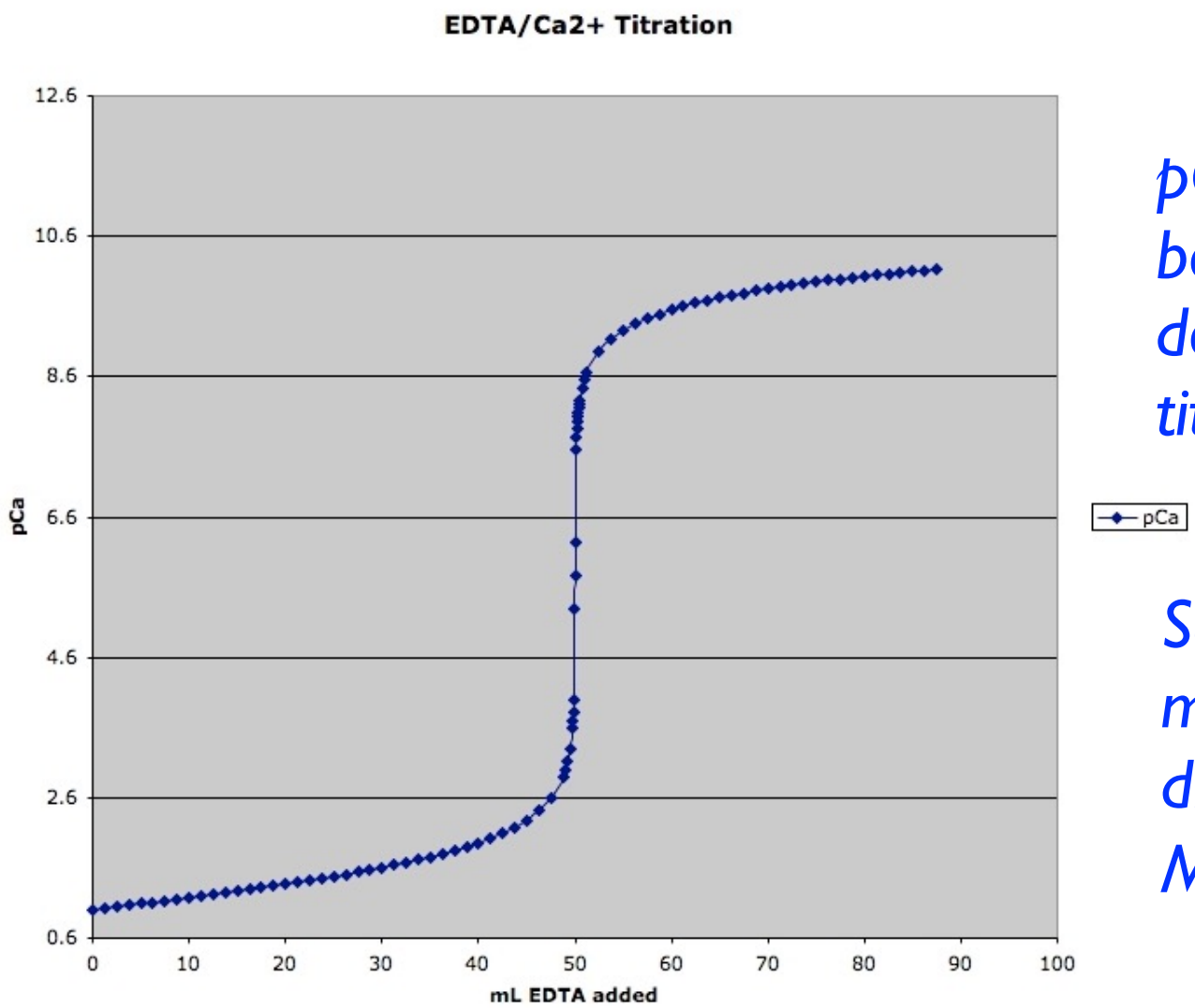
EDTA titrations are always run in basic solutions to insure that there is enough Y^{4-} species

EDTA titrations for metal ions

$$Ca^{2+} + Y^{4-} \rightarrow CaY^{2-} \qquad K_f = 5.01 \times 10^{10}$$

$$Mg^{2+} + Y^{4-} \rightarrow MgY^{2-} \qquad K_f = 4.90 \times 10^{8}$$

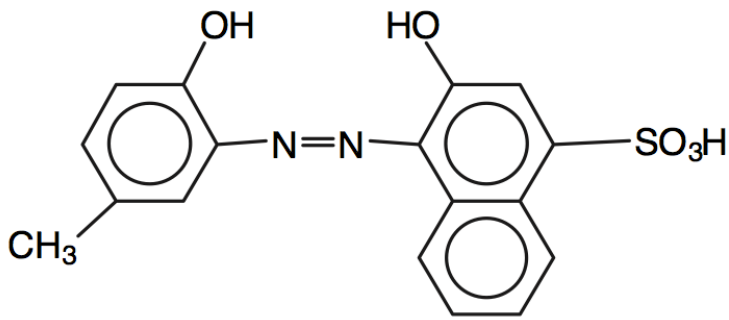
pCa



pCa or pMg can be used to determine the titration endpoint.

Sadly, we cannot measure pCa directly in our M3LC lab.😞

We must use an indicator to detect the endpoint of the EDTA titration



Calmagite (H_3In)

$$In^{3-} \overset{+H^+}{\rightleftharpoons} HIn^{2-} \overset{+H^+}{\rightleftharpoons} H_2In^- \overset{+H^+}{\rightleftharpoons} H_3In$$

(orange) *(blue)*

EDTA will displace weaker ligands -- you will use this process with calmagite to determine the endpoint of an EDTA titration for Mg^{2+}

$$MgIn^- + Y^{4-} \rightleftharpoons MgY^{2-} + In^{3-}$$

(wine-red) *(colorless)* *(??)**

**what you see will depend on pH*

Zn-EDTA Titration: Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a 1.00×10^{-4} M Zn^{2+} solution with a 1.00×10^{-4} M EDTA solution.

What is pZn at the equivalence point?

Log K_f for the ZnY^{2-} complex is 16.5.
Both solutions are buffered to a pH of 10.0.
The alpha fraction for Y^{4-} is 0.355 at a pH of 10.0.

Zn-EDTA Titration: Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a 1.00×10^{-4} M Zn^{2+} solution with a 1.00×10^{-4} M EDTA solution.

Total moles of Zinc $= (1.00 \times 10^{-4}\ M)(0.050L)$

$= 5.0 \times 10^{-6}$ moles

Zn-EDTA Titration: Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a 1.00×10^{-4} M Zn^{2+} solution with a 1.00×10^{-4} M EDTA solution.

Total moles of Zinc = 5.0×10^{-6} moles

Equivalence point volume = 0.100L

Zn-EDTA Titration: Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a 1.00×10^{-4} M Zn^{2+} solution with a 1.00×10^{-4} M EDTA solution.

Total moles of Zinc = 5.0×10^{-6} moles

Equivalence point volume = 0.100L

[ZnY^{2-}] = 5.0×10^{-5} M

We first assume a stoichiometric reaction.

Zn-EDTA Titration: Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a 1.00×10^{-4} M Zn^{2+} solution with a 1.00×10^{-4} M EDTA solution.

Total moles of Zinc = 5.0×10^{-6} moles

Equivalence point volume = 0.100L

[ZnY^{2-}] = 5.0×10^{-5} M

[Zn^{2+}] = ??

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

Then we assume a little bit of free Zinc is formed as required by K_f.

Zn-EDTA Titration: Equivalence Point Calculation

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Total moles of Zinc = 5.0×10^{-6} moles

Equivalence point volume = 0.100L

[ZnY^{2-}] = 5.0×10^{-5} M

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$$[Zn^{2+}] = C_{EDTA}^{tot}$$

For every free Zn^{2+}, there is a free EDTA species

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

Y^{4-} concentration is obtained from the alpha fraction.

Zn-EDTA Titration: Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a 1.00×10^{-4} M Zn^{2+} solution with a 1.00×10^{-4} M EDTA solution.

Total moles of Zinc = 5.0×10^{-6} moles

Equivalence point volume = 0.100L

[ZnY^{2-}] = 5.0×10^{-5} M

[Zn^{2+}] = ??

$$[Zn^{2+}] = \sqrt{\frac{[ZnY^{2-}]}{\alpha_{Y^{4-}} K_f}}$$

Plug everything in and solve for Zn^{2+}...

Zn-EDTA Titration: Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a 1.00×10^{-4} M Zn^{2+} solution with a 1.00×10^{-4} M EDTA solution.

Total moles of Zinc = 5.0×10^{-6} moles

Equivalence point volume = 0.100L

[ZnY^{2-}] = 5.0×10^{-5} M

[Zn^{2+}] = 6.67×10^{-11} M

$$[Zn^{2+}] = \sqrt{\frac{[ZnY^{2-}]}{\alpha_{Y^{4-}} K_f}}$$

pZn = 10.2

$$\alpha_{Y^{4-}} K_f = K_f'$$

conditional formation constant

And we are done!

Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

You would like to perform a titration of 50.00 mL of a 1.00 x 10^{-4} M Zn^{2+} solution with a 1.00 x 10^{-4} M EDTA solution.

Both solutions are buffered to a pH of 10.0 using a 0.100M ammonia buffer.

a) How much total free Zn is left in solution?

b) What is the Zn^{2+} concentration?

Zinc Hydroxide

$$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_{2(s)}$$

Solubility product $K_{sp} = 3.0 \times 10^{-17}$

$$K_{sp} = [Zn^{2+}][OH^{-}]^2$$

At pH=10, $[Zn^{2+}]$ = ??

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At pH=10, $[Zn^{2+}] = K_{sp} / [OH^{-}]^2$

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Solubility product $K_{sp} = 3.0\times10^{-17}$

$$K_{sp} = [Zn^{2+}][OH^{-}]^2$$

At pH=10, $[Zn^{2+}] = K_{sp} / [OH^{-}]^2$

$= (3.0\times10^{-17}) / (1.0\times10^{-4})^2$

$= 3.0\times10^{-9}$ M

This is the maximum free Zinc concentration.

Ammonia Buffer Solution

$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$ $pK_b = 4.74$

$[NH_3]_{total} = 0.100M$

At pH=10, $[NH_3]$ = ??

Ammonia Buffer Solution

$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$ $\qquad pK_b = 4.74$

$[NH_3]_{total} = 0.100M$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$[NH_3] = \alpha_{NH_3} C^{tot}$$

$$\alpha_{NH_3} = \left[1 + \frac{K_b}{[OH^-]}\right]^{-1}$$

At pH=10:

$[NH_3]$ = 0.0846 M

Zinc Complexation

Zinc - Ammonia Complexation

1. Zinc-ammonia complexation

$Zn^{2+} + NH_3 = Zn(NH_3)^{2+}$	$K_1 = 180$	$\beta_1 = K_1 = 180$
$Zn(NH_3)^{2+} + NH_3 = Zn(NH_3)_2^{2+}$	$K_2 = 220$	$\beta_2 = K_1K_2 = 3.96 \times 10^4$
$Zn(NH_3)_2^{2+} + NH_3 = Zn(NH_3)_3^{2+}$	$K_3 = 250$	$\beta_3 = K_1K_2K_3 = 9.90 \times 10^6$
$Zn(NH_3)_3^{2+} + NH_3 = Zn(NH_3)_4^{2+}$	$K_4 = 110$	$\beta_4 = K_1K_2K_3K_4 = 1.09 \times 10^9$

$$\alpha_{Zn^{2+}} = \frac{1}{1 + K_1[NH_3] + K_1K_2[NH_3]^2 + K_1K_2K_3[NH_3]^3 + K_1K_2K_3K_4[NH_3]^4}$$

At $[NH_3] = 0.0846M$, $\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$

Zinc - Ammonia Complexation

At a TOTAL Zinc concentration of 1.00×10^{-4} M:

$$[Zn^{2+}] = \alpha_{Zn^{2+}} [Zn^{2+}]^{tot}$$

$$[Zn^{2+}] = (1.61 \times 10^{-5})(1.00 \times 10^{-4})$$

$$[Zn^{2+}] = 1.61 \times 10^{-9} \text{ M}$$

Therefore: no precipitation!

Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

You would like to perform a titration of 50.00 mL of a 1.00 x 10^{-4} M Zn^{2+} solution with a 1.00 x 10^{-4} M EDTA solution.

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Both solutions are buffered to a pH of 10.0 using a 0.100M ammonia buffer.

At pH=10: $\alpha_{Y^{4-}} = 0.355$

$$\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$$

For ZnY^{4-} $\log K_f = 16.5$

Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

You would like to perform a titration of 50.00 mL of a 1.00 x 10^{-4} M Zn^{2+} solution with a 1.00 x 10^{-4} M EDTA solution.

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$$\alpha_{Y^{4-}} = 0.355$$

$$\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$$

$$\log K_f = 16.5$$

We assume a stoichiometric reaction.

Total moles of Zinc = 5.0 x 10^{-6} moles

Equivalence point volume = 0.100L

[ZnY^{2-}] = 5.0 x 10^{-5} M

Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

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$$\alpha_{Y^{4-}} = 0.355$$

$$\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$$

$$\log K_f = 16.5$$

$$[ZnY^{2-}] = 5.0 \times 10^{-5}\ M$$

a) How much total free Zn is left in solution?

Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

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$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$$\alpha_{Y^{4-}} = 0.355$$

$$\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$$

$$\log K_f = 16.5$$

$$[ZnY^{2-}] = 5.0 \times 10^{-5}\ M$$

a) How much total free Zn is left in solution?

$$C_{Zn}^{tot} = C_{EDTA}^{tot}$$

$$[Zn^{2+}] = \alpha_{Zn^{2+}} C_{Zn}^{tot}$$

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

$$C_{Zn}^{tot} = \sqrt{\frac{[ZnY^{2-}]}{\alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f}}$$

Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

You would like to perform a titration of 50.00 mL of a 1.00 x 10^{-4} M Zn^{2+} solution with a 1.00 x 10^{-4} M EDTA solution.

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$$\alpha_{Y^{4-}} = 0.355$$

$$\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$$

$$\log K_f = 16.5$$

$$[ZnY^{2-}] = 5.0 \times 10^{-5}\ M$$

a) How much total free Zn is left in solution?*

$$C_{Zn}^{tot} = \sqrt{\frac{[ZnY^{2-}]}{\alpha_{Zn^{2+}}\alpha_{Y^{4-}}K_f}}$$

$$C_{Zn}^{tot} = 1.66 \times 10^{-8}\ M$$

$$\alpha_{Zn^{2+}}\alpha_{Y^{4-}}K_f = K_f''$$

double conditional formation constant

**free means not in the ZnY^{2-} complex*

Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

You would like to perform a titration of 50.00 mL of a 1.00 x 10^{-4} M Zn^{2+} solution with a 1.00 x 10^{-4} M EDTA solution.

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$$\alpha_{Y^{4-}} = 0.355$$

$$\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$$

$$\log K_f = 16.5$$

$$[ZnY^{2-}] = 5.0 \times 10^{-5}\ M$$

$$C_{Zn}^{tot} = 1.66 \times 10^{-8}\ M$$

b) What is the Zn^{2+} concentration?

Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

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$$\alpha_{Y^{4-}} = 0.355$$

$$\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$$

$$\log K_f = 16.5$$

$$[ZnY^{2-}] = 5.0 \times 10^{-5}\ M$$

$$C_{Zn}^{tot} = 1.66 \times 10^{-8}\ M$$

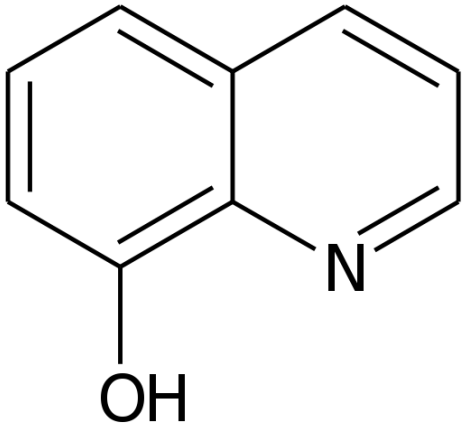
b) What is the Zn^{2+} concentration?

$$[Zn^{2+}] = \alpha_{Zn^{2+}} C_{Zn}^{tot} = (1.61 \times 10^{-5})(1.66 \times 10^{-8}\ M)$$

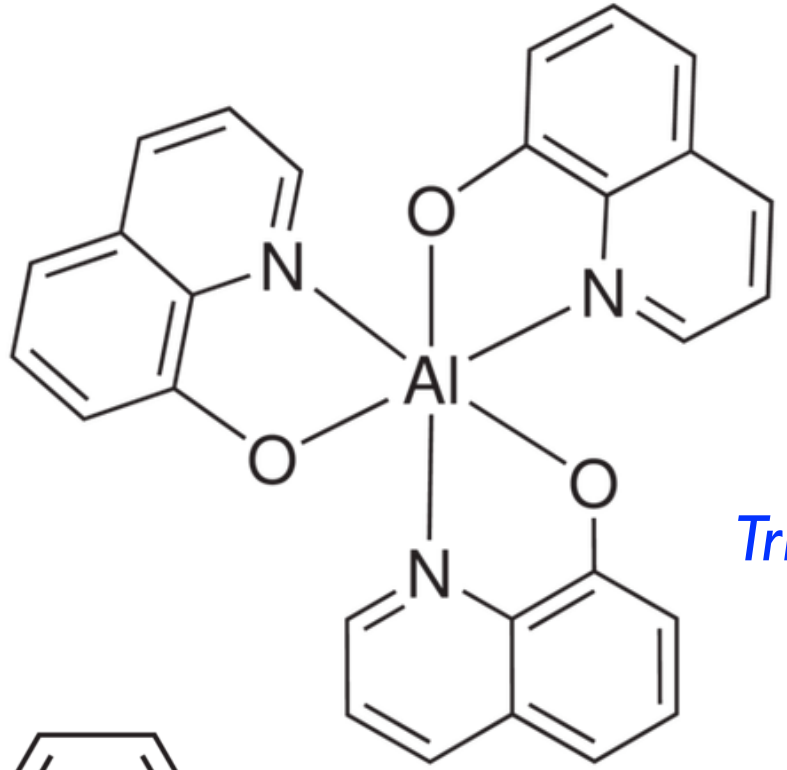
$$[Zn^{2+}] = 2.67 \times 10^{-13}\ M$$

pZn = 12.6

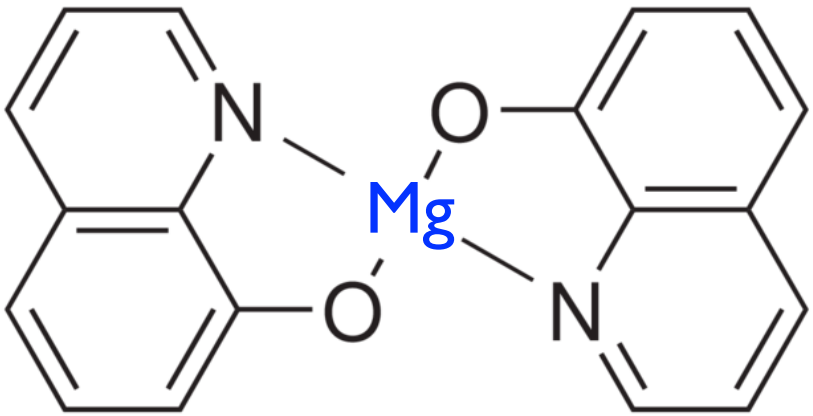
Hydroxyquinoline: a metal chelator that fluoresces upon binding!



8-hydroxyquinoline

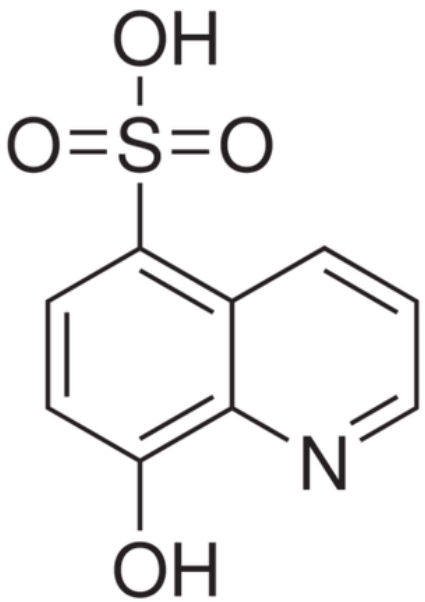


Trivalent Cations



Divalent Cations

Hydroxyquinoline: a metal chelator that fluoresces upon binding!



8-hydroxyquinoline-5-sulfonic Acid

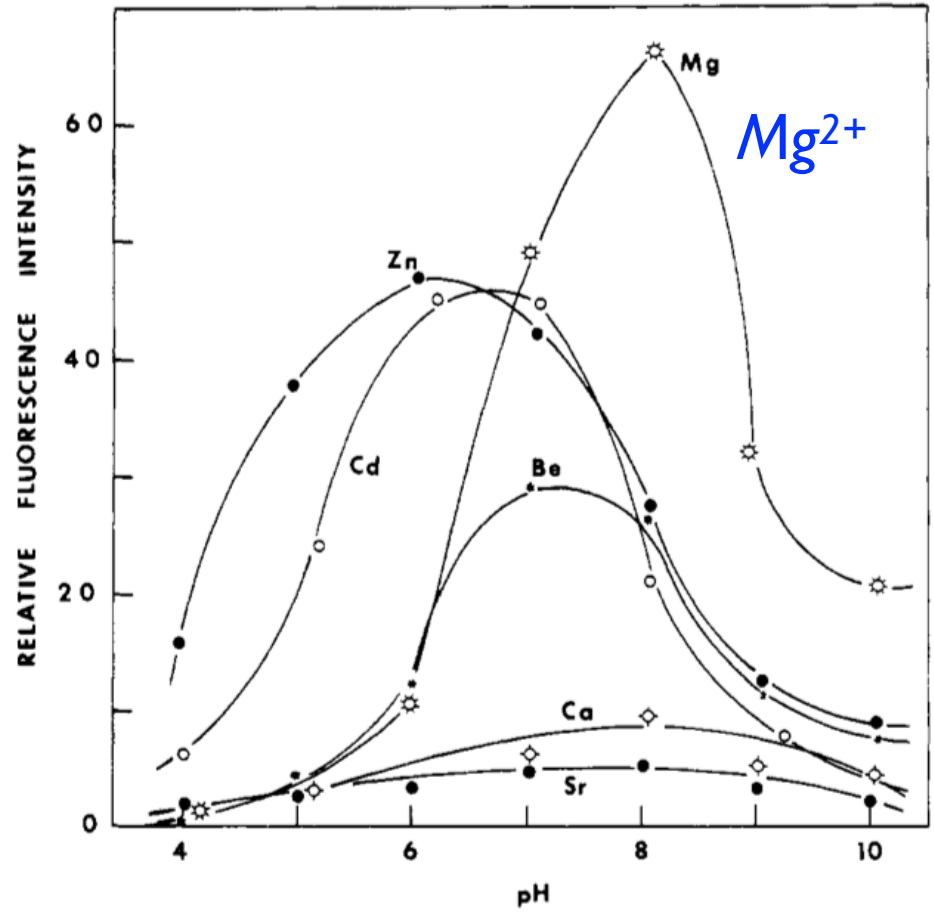


Figure 1. pH dependence of the fluorescnece intensities of group II metal–HQS chelates: Cd, 2 μM; all other metals in this and following figures, 20 μM; HQS, 1 mM.

Fluorometric Detection of Mg^{2+} in Seawater