Metal-Ligand Complexation Equilibria

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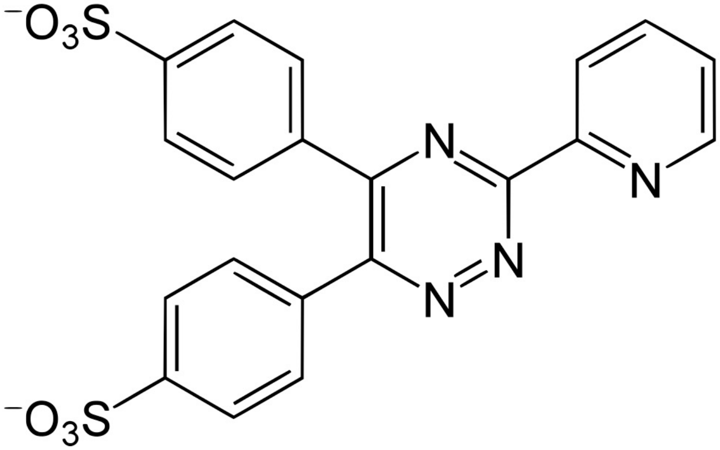
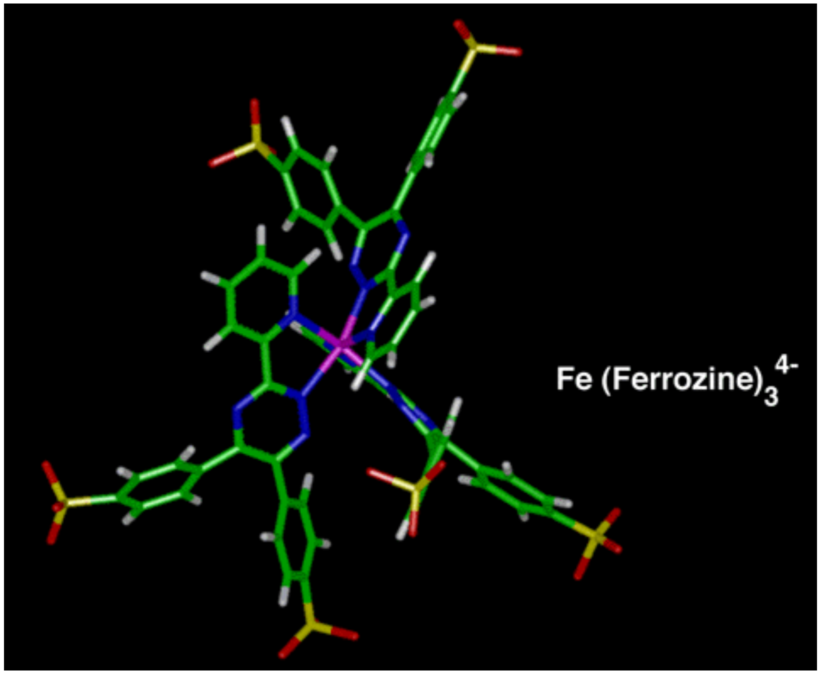
We already used metal complexation in Week 2 for the Fe Colorimetry Experiment:

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



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

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

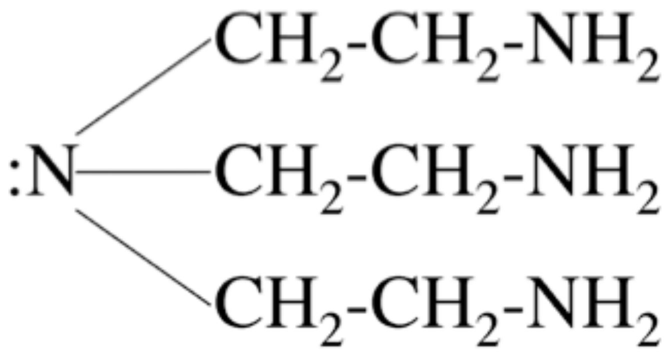
$$\alpha_{Zn^{2+}} = \frac{1}{1 + K_1[NH_3] + K_1K_2[NH_3]^2 + K_1K_2K_3[NH_3]^3 + K_1K_2K_3K_4[NH_3]^4}$$

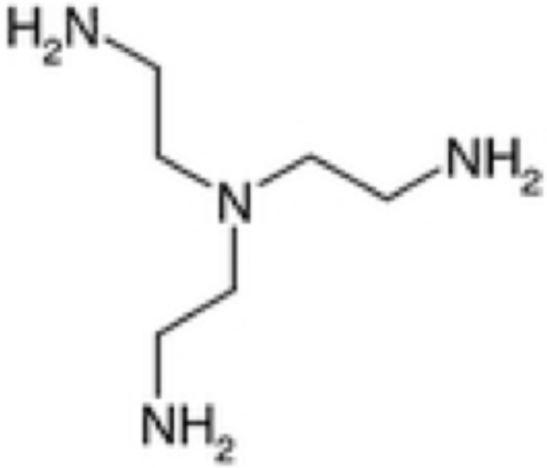
Therefore, many species co-exist in solution!

2. Zinc-tren complexation

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

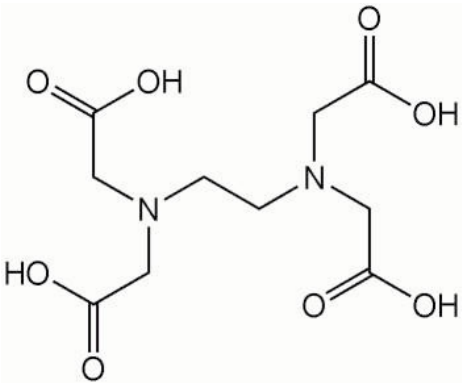
tren = triaminotriethylamine





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

EDTA Metal Ion Complexation Equilibria



Ethylene Diamine Tetra-acetic Acid (H_4Y)

EDTA - the world's best metal ion chelator

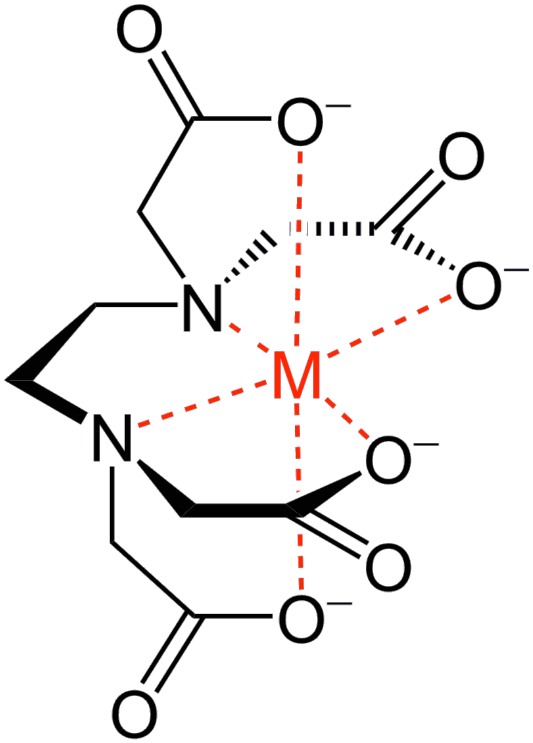
Metal complexation reactions with Y^{4-}:

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

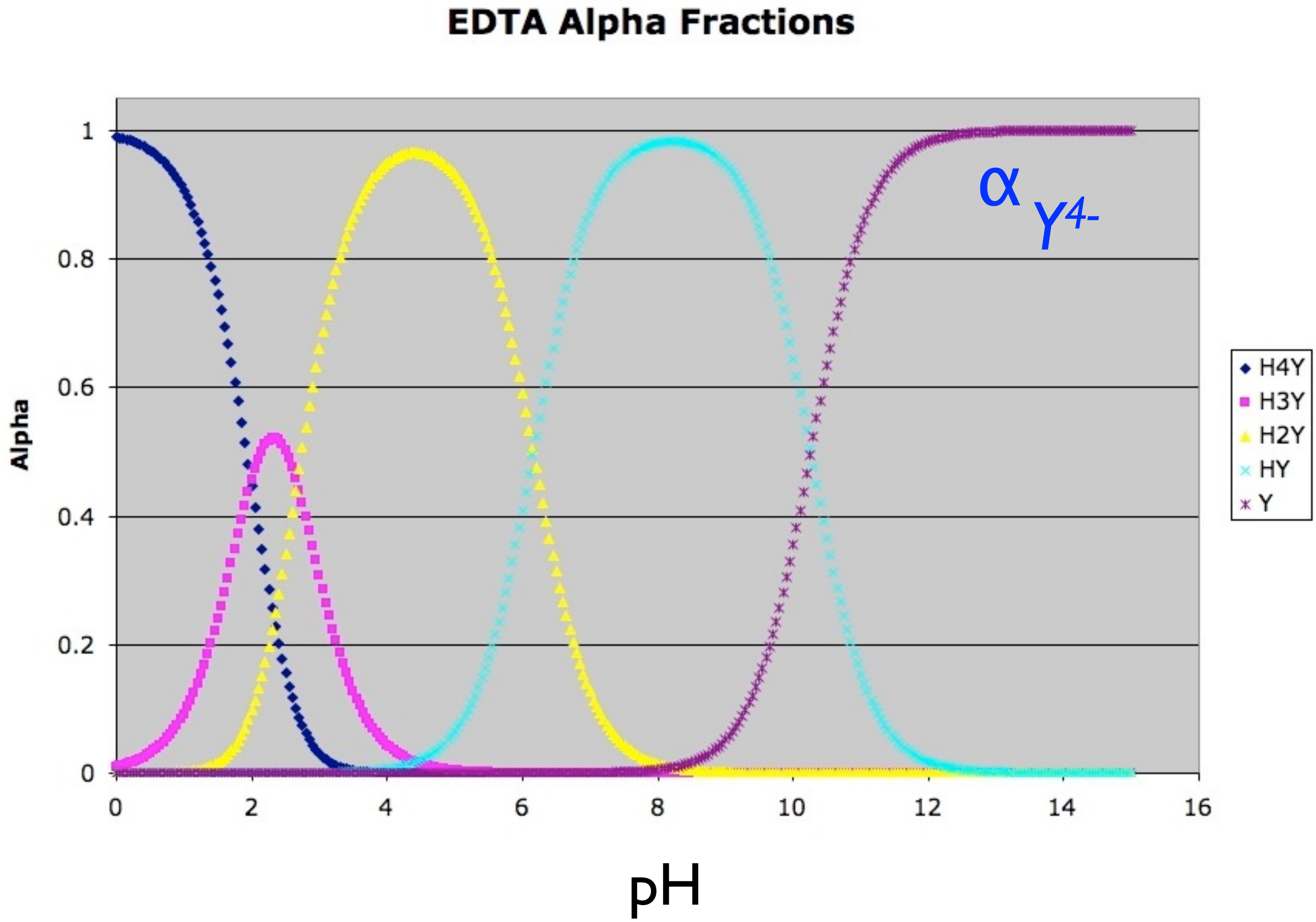
Metal Ion	log K_f
Ag^+	7.32
Mg^{2+}	8.69
Ca^{2+}	10.70
Co^{2+}	16.31
Cd^{2+}	16.46
Al^{3+}	15.89
Fe^{3+}	25.10
V^{3+}	25.90

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-}:

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

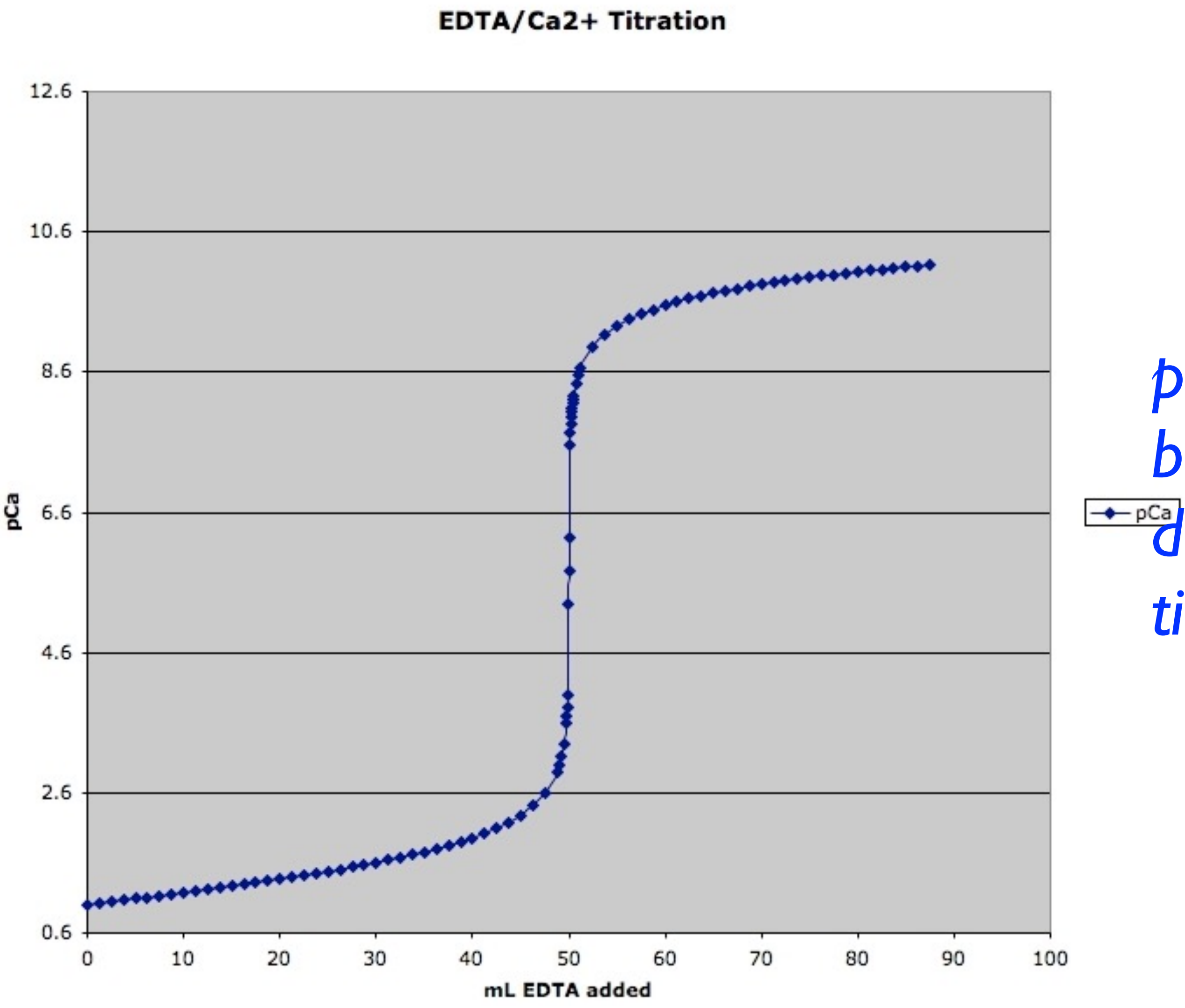
α_{Y4-} is equal to 0.35 at a pH of 10.

EDTA titrations for metal ions

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

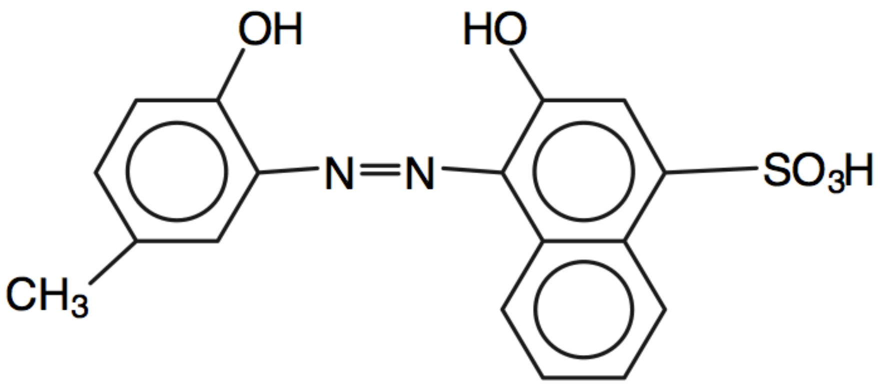
$Mg^{2+} + Y^{4-} \rightarrow MgY^{2-}$ $K_f = 4.90 \times 10^{8}$

pCa



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

EDTA titrations for metal ions

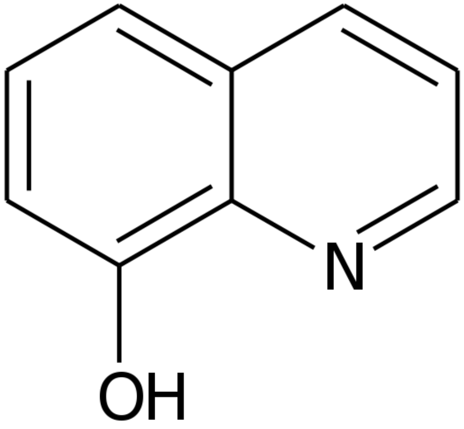


Calmagite (H_3In)

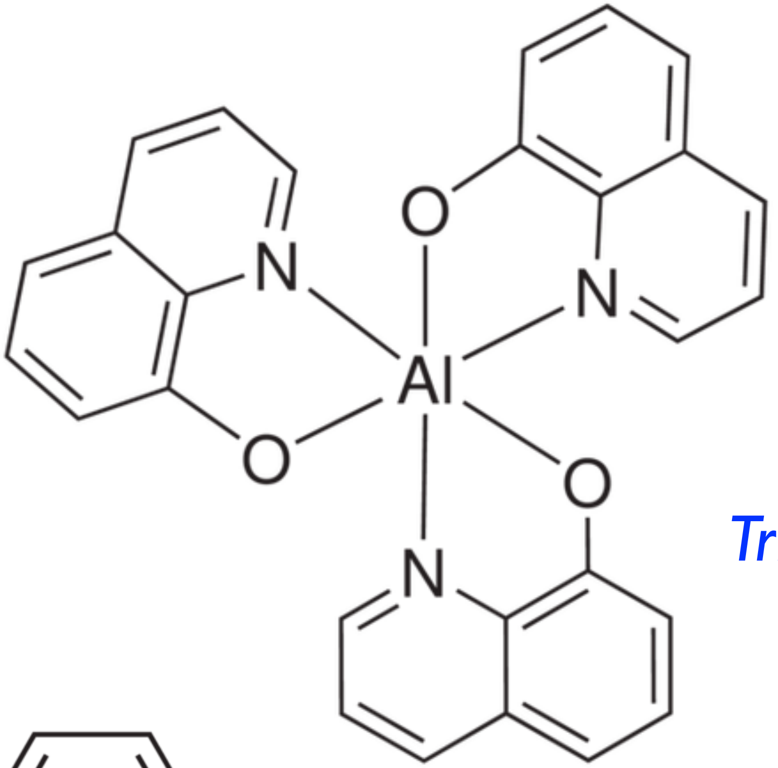
$MgIn^-$	+	HY^{3-}	$\rightleftharpoons$	MgY^{2-}	+	HIn^{2-}
metal ion/ indicator complex		titrant		metal ion/ EDTA complex		free indicator
(wine-red)		(colorless)		(colorless)		(blue)

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

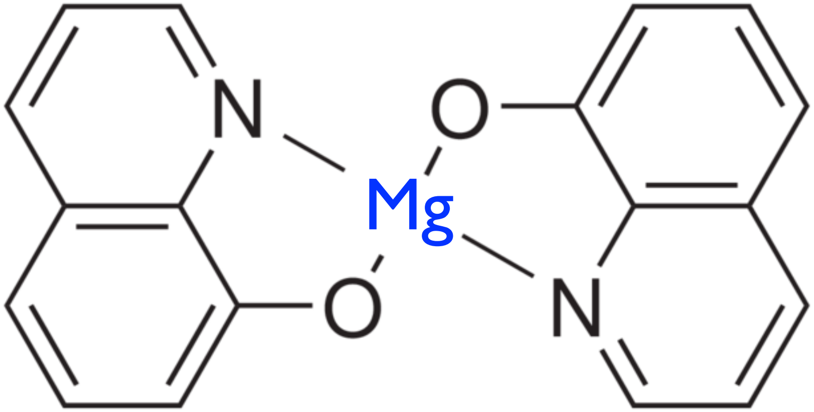
Hydroxyquinoline: a metal chelator that fluoresces upon binding!



8-hydroxyquinoline

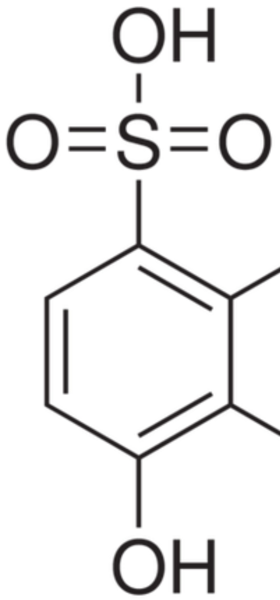


Trivalent Cations



Divalent Cations

Hydroxyquinoline: a metal chelator that fluoresces upon binding!



8-hydroxyquinoline-5-sulfonic Acid

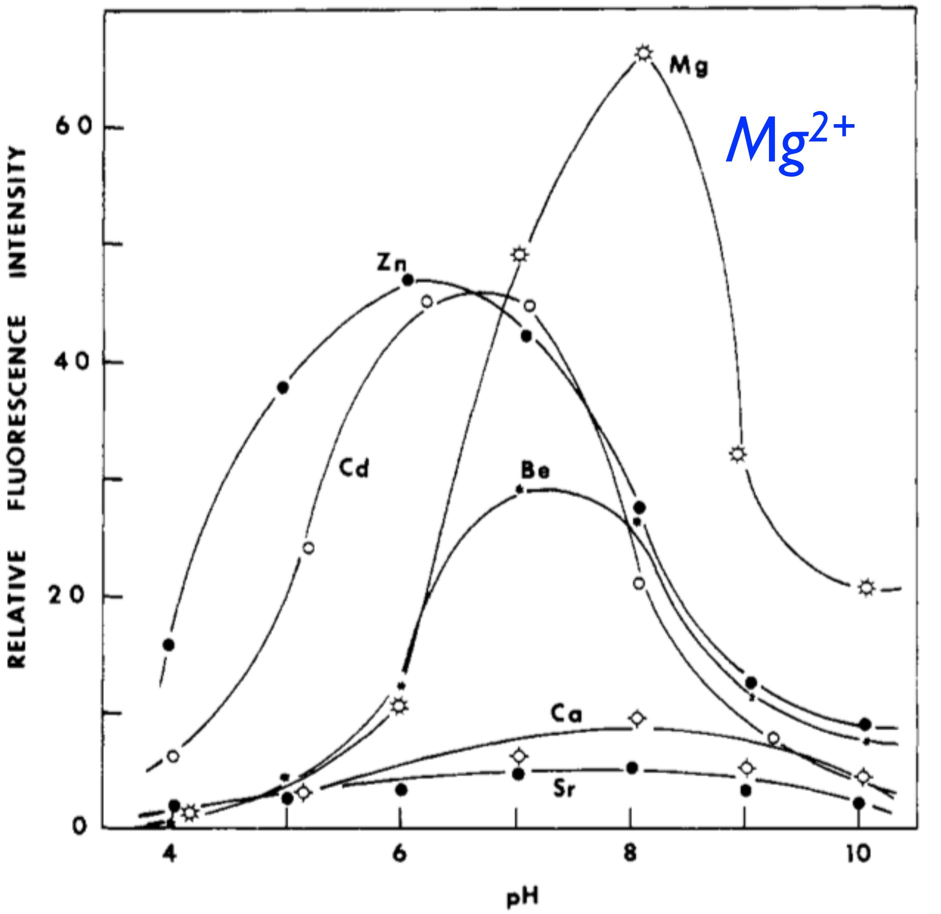
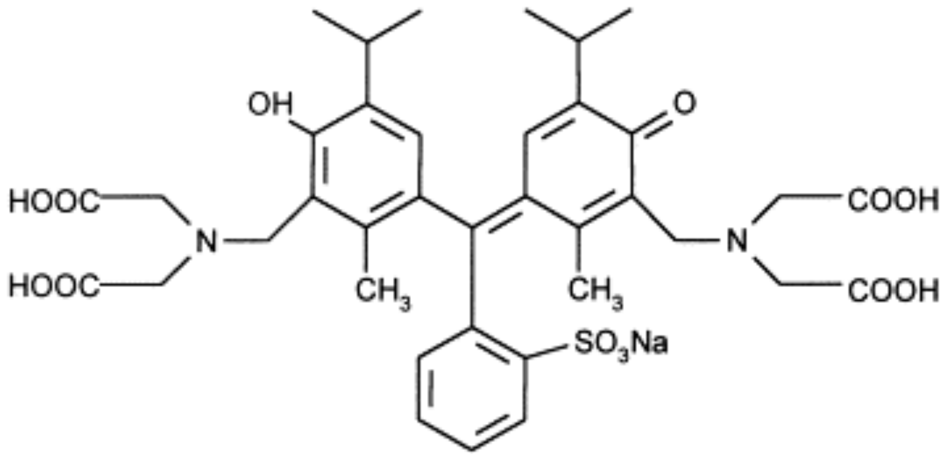


Figure 1. pH dependence of the fluorescnece intensities of group II metal–HQS chelates: Cd, 2 μM; all other metals in this and following figures, 20 μM; HQS, 1 mM.

Fluorometric Detection of Mg^{2+} in Seawater

Another example:

Ba^{2+} forms a complex with methylthymol blue (MTB^{5-}):



MTB^{5-}

MTB: abs. max @ 460 nm

Ba-MTB complex: abs. max @ 610 nm

Some of you will use barium-MTB complexation to measure sulfate concentrations in seawater!

Metal Complexation Formation Constants

Barium-MTB Complexation Equilibrium:

$$Ba^{2+} + MTB^{5-} \leftrightarrow BaMTB^{3-} \qquad K_f$$

$$K_f = \frac{[BaMTB^{3-}]}{[Ba^{2+}][MTB^{5-}]}$$

K_f is the Ba-MTB Formation Constant

$K_f \approx 10^5$

Alpha Fractions for free and complexed Ba^{2+}

$$C_{Ba}^{tot} = [Ba^{2+}] + [BaMTB^{3-}]$$

The total Barium Concentration in solution is conserved.

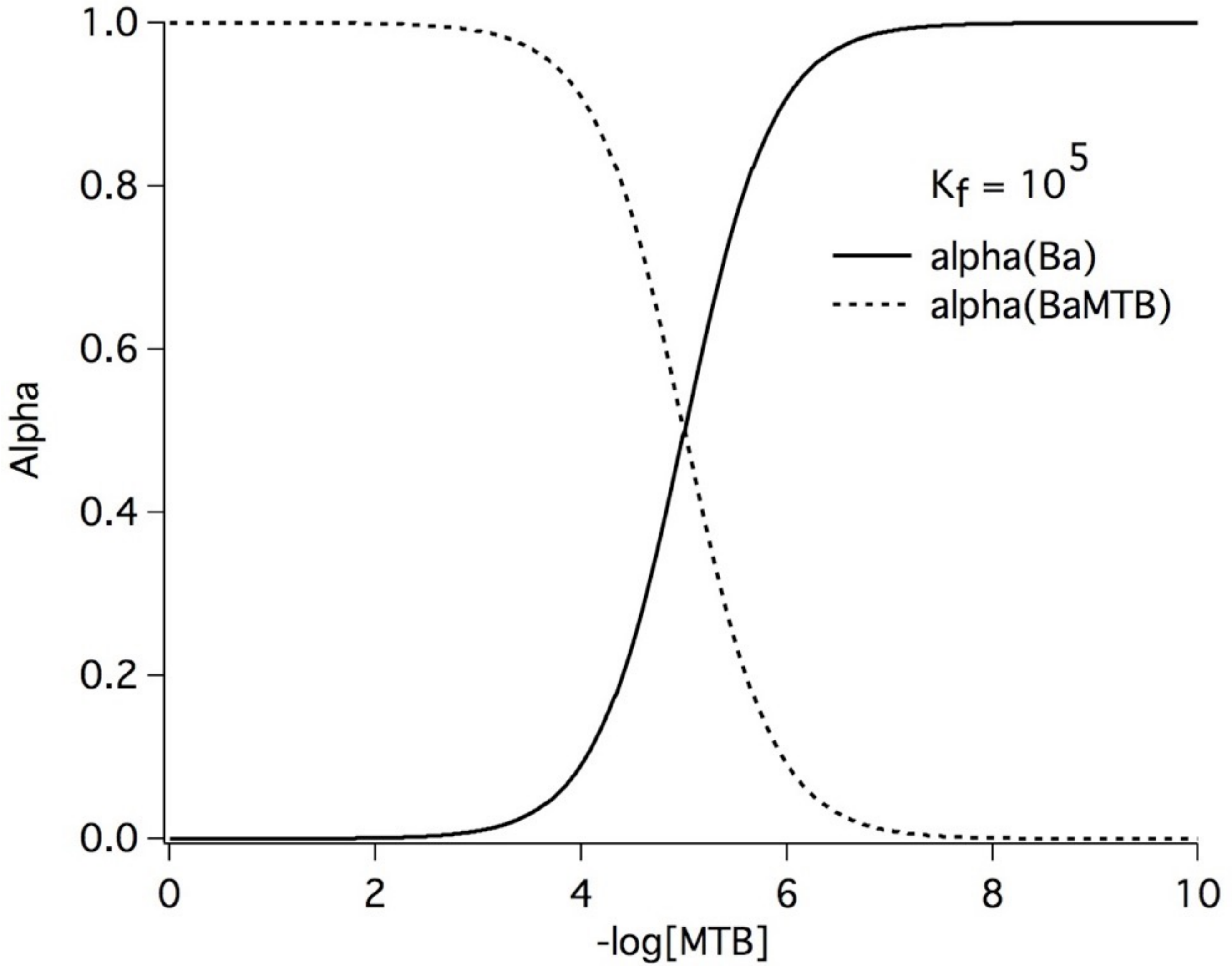
$$\alpha_{Ba^{2+}} = \frac{[Ba^{2+}]}{C_{Ba}^{tot}} = \frac{1}{1 + K_f[MTB^{5-}]}$$

Alpha Fractions!

$$\alpha_{BaMTB^{4-}} = \frac{[BaMTB^{3-}]}{C_{Ba}^{tot}} = \frac{K_f[MTB^{5-}]}{1 + K_f[MTB^{5-}]}$$

$$\alpha_{Ba^{2+}} + \alpha_{BaMTB^{3-}} = 1$$

Alpha Fractions for free and complexed Ba^{2+}



The ligand concentration ([MTB]) determines the speciation.