

CEE 680: Water Chemistry

Lecture #31

Coordination Chemistry: Case Studies: EDTA,
detergents

(Stumm & Morgan, Chapt.6: pg.317-319)

Benjamin; Chapter 8.1-8.6

EDTA Complexation

- $M^{+n} + Y^{-4} = MY^{n-4}$
- $K = [MY^{n-4}]/[M^{+n}][Y^{-4}]$

Metal	Log K	Metal	Log K
K (+I)	0.8	Pb (+II)	18.04
Na (+I)	1.66	Sn (+II)	18.3
Li (+I)	2.79	Ni (+II)	18.62
Ba (+II)	7.86	Cu (+II)	18.80
Mg (+II)	8.79	Hg (+II)	21.7
Ca (+II)	10.69	Al (+III)	16.3
Cr (+II)	13.6	Cr (+III)	23.4
Mn (+II)	13.87	Mn (+III)	25.3
Fe (+II)	14.32	Fe (+III)	25.1

EDTA Protonation

- Acidic groups

- Carboxylic groups

- $pK_1 = 0.0$ $pK_2 = 1.5$ $pK_3 = 2.0$ $pK_4 = 2.66$

- Amine groups

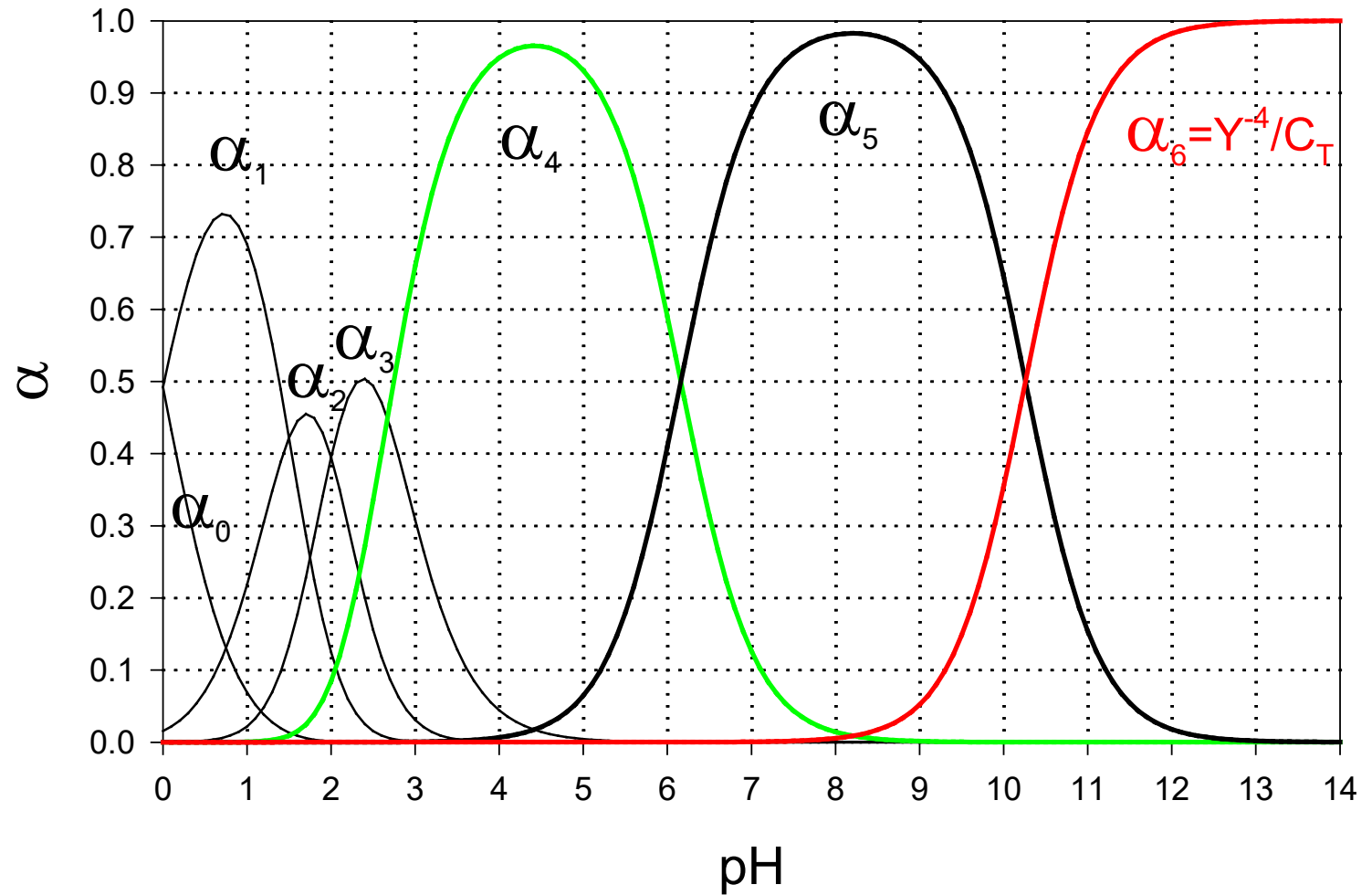
- $pK_5 = 6.16$ $pK_6 = 10.24$

$$\alpha_6 \equiv \frac{[Y^{-4}]}{\sum_{n=0-6} H_n Y^{n-4}}$$

- Major ligand form: Y^{-4}

- $\alpha_6 = 1/\{[H]^6/K_1K_2K_3K_4K_5K_6 + [H]^5/K_2K_3K_4K_5K_6 + [H]^4/K_3K_4K_5K_6 + [H]^3/K_4K_5K_6 + [H]^2/K_5K_6 + [H]/K_6 + 1\}$

EDTA: Alpha diagram



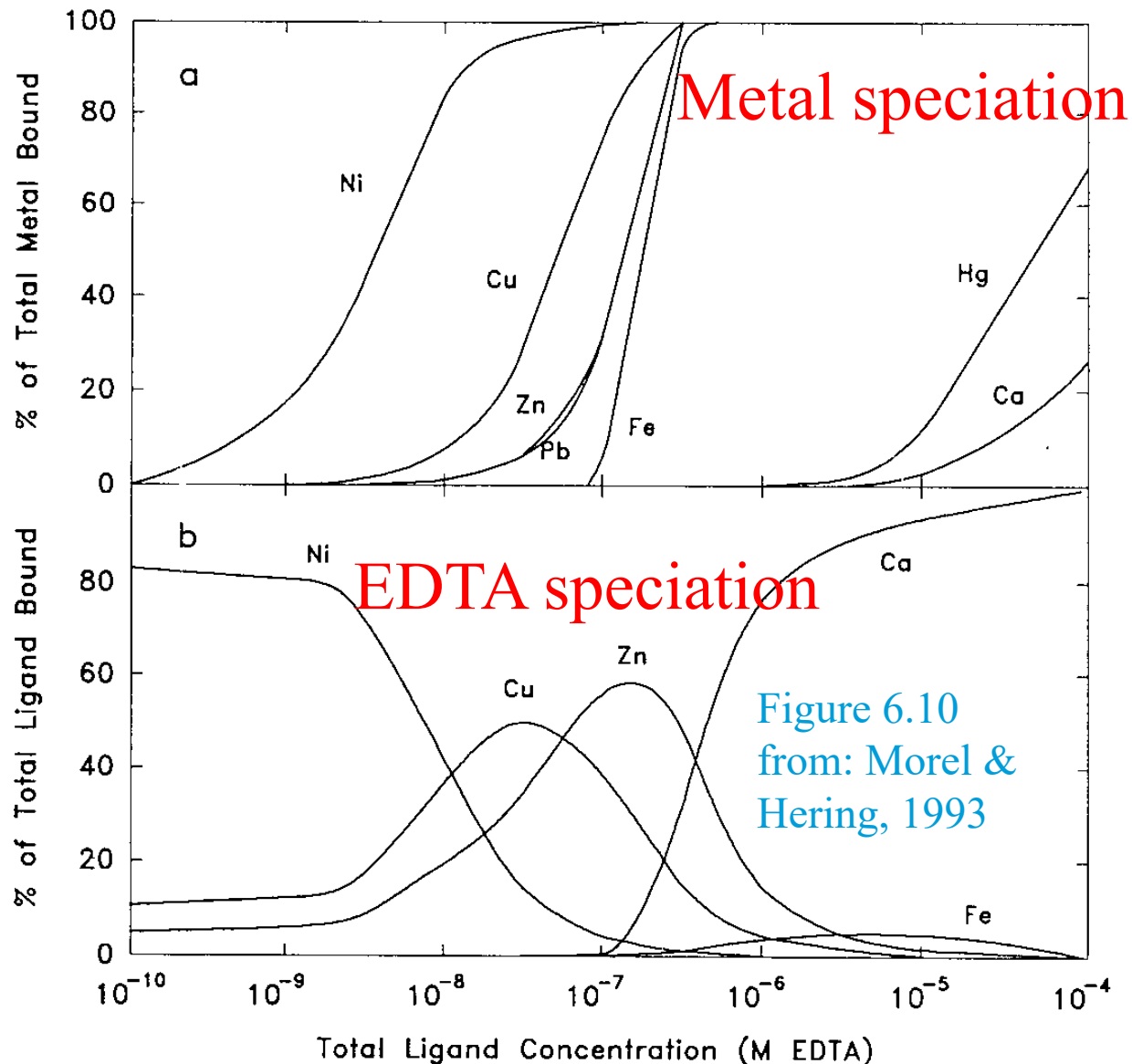
Me:EDTA speciation

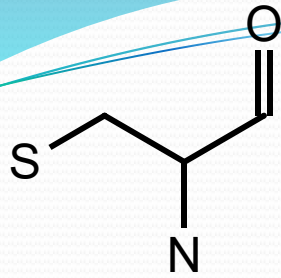
- Titration of a model fresh water with EDTA

- Fixed pH = 8.10

- Total concentration

- $\text{Ca}_T = 3.7 \times 10^{-4} \text{ M}$
- $\text{Mg}_T = 1.6 \times 10^{-4} \text{ M}$
- $\text{K}_T = 6 \times 10^{-5} \text{ M}$
- $\text{Na}_T = 2.8 \times 10^{-4} \text{ M}$
- $\text{Fe(III)}_T = 5 \times 10^{-7} \text{ M}$
- $\text{Cu}_T = 5 \times 10^{-8} \text{ M}$
- $\text{Hg}_T = 10^{-9} \text{ M}$
- $\text{Zn}_T = 1.5 \times 10^{-7} \text{ M}$
- $\text{Ni}_T = 5 \times 10^{-9} \text{ M}$
- $\text{Pb}_T = 10^{-9} \text{ M}$
- $[\text{CO}_3]_T = 10^{-3} \text{ M}$
- $[\text{SO}_4]_T = 10^{-4} \text{ M}$
- $\text{Cl}_T = 2 \times 10^{-4} \text{ M}$

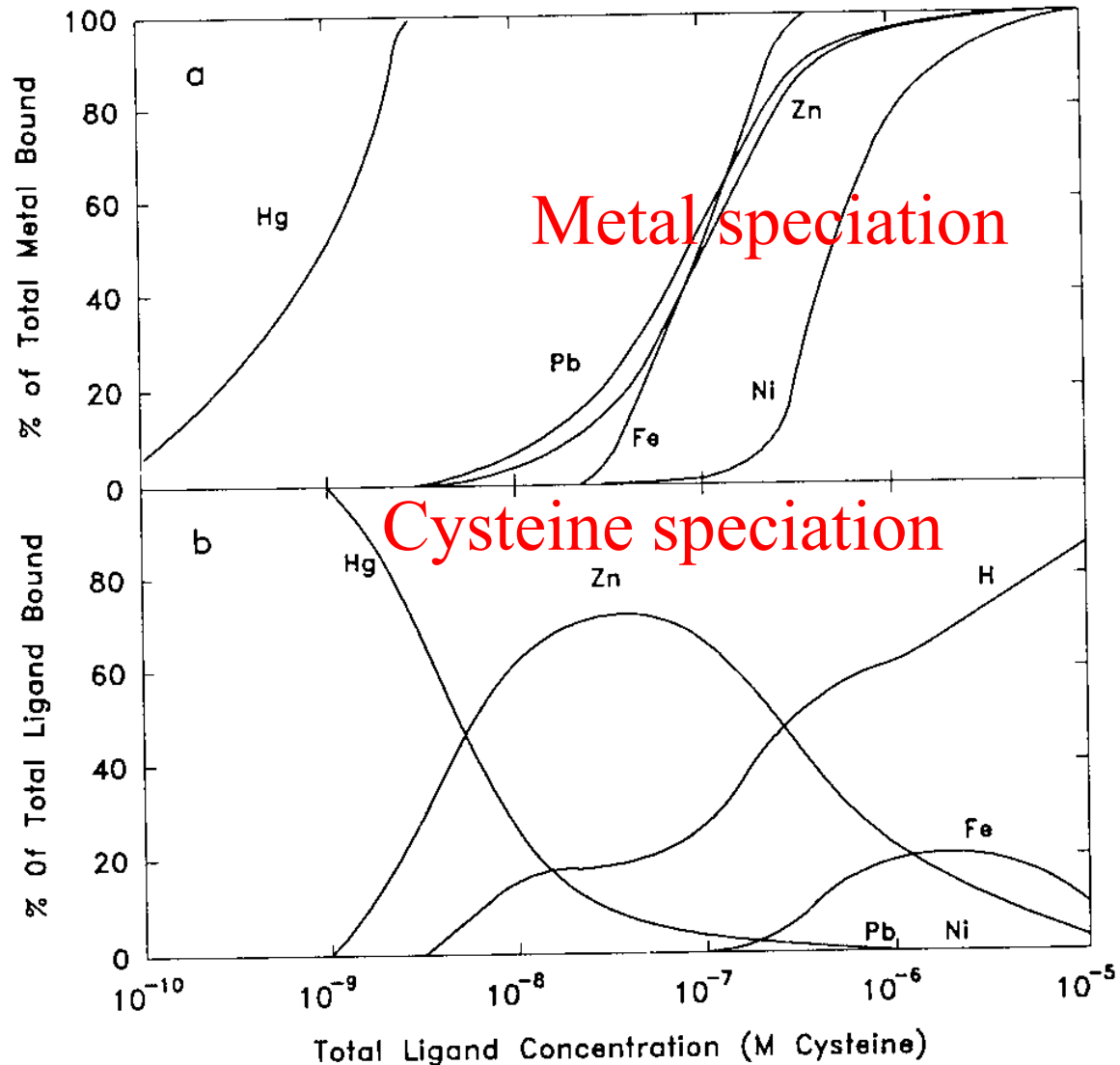




Me: Cysteine speciation

- Titration of a model fresh water with cysteine
- Same concentrations as in previous EDTA figure
 - Except no Cu

Figure 6.12 from:
Morel & Hering,
1993



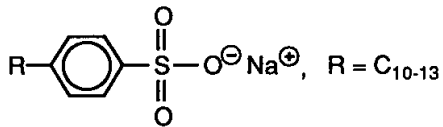
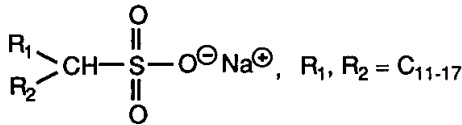
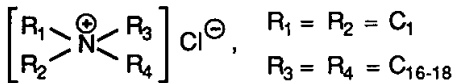
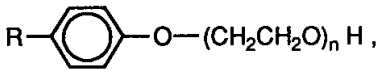
Complexation Problems

- Metal-Simple Monodentate Ligand
 - Example: Al-F system
 - Can be solved graphically
- Metal-Multidentate Ligand (1:1 complex)
 - Must consider Ligand protonation
 - Example: Cu-NTA system
 - Can be solved algebraically
- Metal-Multi-ligand system
 - Example: Pb-OH-CO₃-citrate system
 - Best to use computer solution (MINEQL)

Surfactants

- Anionics
 - 65%
- Cationics
 - 7%
- Nonionics
 - 28%

TABLE 2.6 Examples of Commercially Important Surfactants^a

Common Name of Surfactant Class (Acronym)	General Structure
<i>Anionic Surfactants</i>	
Soaps	$R-CH_2-COO^{\ominus}Na^{\oplus}$, $R = C_{10-16}$
Linear alkylbenzene sulfonates (LAS)	 $R = C_{10-13}$
Secondary alkyl sulfonates (SAS)	 $R_1, R_2 = C_{11-17}$
Fatty alcohol sulfates (Alkyl sulfates, FAS)	$R-CH_2-O-SO_3^{\ominus}Na^{\oplus}$, $R = C_{11-17}$
<i>Cationic Surfactants</i>	
Quaternary ammonium chloride (QAC)	 $R_1 = R_2 = C_1$ $R_3 = R_4 = C_{16-18}$
<i>Nonionic Surfactants</i>	
Alkylphenol polyethyleneglycol ethers (APEO)	 $R = C_{8-12}$ $n = 5-10$
Fatty alcohol polyethyleneglycol ethers (AEO)	$R-CH_2-O-(CH_2CH_2O)_n H$, $R = C_{7-17}$ $n = 3-15$

^aFrom Piorr (1987).

From: Schwarzenbach et al., 1993, pg. 38

Powdered Detergents

● Typical Formulation

Component	Examples
Anionic surfactants	Alkylbenzene sulfonates Fatty alcohol sulfates Fatty alcohol ether sulfates Alpha-olefin sulfonates
Nonionic surfactants	Alkyl and nonylphenyl poly(ethylene glycol) ethers
Suds-controlling agents	Soaps, silicon oils, paraffins
Foam boosters	Fatty acid monoethanol amides
Chelaters (builders)	Sodium tripolyphosphate
Ion exchange	Zeolite 4A, poly(acrylic acids)
Alkalies	Sodium carbonate
Cobuilders	Sodium citrate Sodium Nitrilotriacetate ← NTA
Bleaching agents	Sodium perborate
Bleach activators	Tetraacetythylenediamine
Bleach stabilizers	Ethylenediaminetetraacetate
Fabric softeners	Quaternary ammonium compounds
Antiredeposition agents	Cellulose ethers
Enzymes	Proteases, amylases
Optical brighteners	Stilbene derivatives
Anticorrosion agents	Sodium silicate
Fragrances	
Dyes and blueing Agents	
Formulation aids	
Fillers and water	Sodium sulfate

Liquid Detergents

Component	Examples
Anionic surfactants	Alkylbenzene sulfonates Fatty alcohol ether sulfates Soaps
Nonionic surfactants	poly(ethylene glycol) ethers, Soaps
Suds-controlling agents	Soaps
Foam boosters	Fatty acid alkanolamides
Enzymes	Proteases
Builders	Potassium diphosphate sodium tripolyphosphate sodium citrate sodium silicate
Formulation aids	Xylene sulfonates, ethanol, propylene glycol
Optical brighteners	Stilbene derivatives
Stabilizers	Triethanolamine
Fabric softeners	Quaternary ammonium salts
Fragrances	
Dyes	
Water	



- To next lecture