Lecture #31

Coordination Chemistry: Case Studies: EDTA, detergents

(Stumm & Morgan, Chapt.6: pg.317-319)
Benjamin; Chapter 8.1-8.6

EDTA Complexation

- \( \text{M}^{+n} + \text{Y}^{-4} = \text{MY}^{n-4} \)
- \( K = \frac{[\text{MY}^{n-4}]}{[\text{M}^{+n}][\text{Y}^{-4}]} \)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Log K</th>
<th>Metal</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>K (+I)</td>
<td>0.8</td>
<td>Pb (+II)</td>
<td>18.04</td>
</tr>
<tr>
<td>Na (+I)</td>
<td>1.66</td>
<td>Sn (+II)</td>
<td>18.3</td>
</tr>
<tr>
<td>Li (+I)</td>
<td>2.79</td>
<td>Ni (+II)</td>
<td>18.62</td>
</tr>
<tr>
<td>Ba (+II)</td>
<td>7.86</td>
<td>Cu (+II)</td>
<td>18.80</td>
</tr>
<tr>
<td>Mg (+II)</td>
<td>8.79</td>
<td>Hg (+II)</td>
<td>21.7</td>
</tr>
<tr>
<td>Ca (+II)</td>
<td>10.69</td>
<td>Al (+III)</td>
<td>16.3</td>
</tr>
<tr>
<td>Cr (+II)</td>
<td>13.6</td>
<td>Cr (+III)</td>
<td>23.4</td>
</tr>
<tr>
<td>Mn (+II)</td>
<td>13.87</td>
<td>Mn (+III)</td>
<td>25.3</td>
</tr>
<tr>
<td>Fe (+II)</td>
<td>14.32</td>
<td>Fe (+III)</td>
<td>25.1</td>
</tr>
</tbody>
</table>
EDTA Protonation

- Acidic groups
  - Carboxylic groups
    - $pK_1 = 0.0$  $pK_2 = 1.5$  $pK_3 = 2.0$  $pK_4 = 2.66$
  - Amine groups
    - $pK_5 = 6.16$  $pK_6 = 10.24$
- Major ligand form: $Y^{-4}$
  - $\alpha_6 \equiv \frac{[Y^{-4}]}{\sum_{n=0}^{6} H^+_n Y^{n-4}}$
  - $\alpha_6 = \frac{1}{[[H^+]^9/K_1K_2K_3K_4K_5K_6 + [H^+]^5/K_2K_3K_4K_5K_6 + [H^+]^4/K_3K_4K_5K_6 + [H^+]^3/K_4K_5K_6 + [H^+]^2/K_5K_6 + [H^+]K_6 + 1]}$
Titration of a model fresh water with EDTA

- Fixed pH = 8.10
- Total concentrations
  - $\text{Ca}^T = 3.7 \times 10^{-4} \text{ M}$
  - $\text{Mg}^T = 1.6 \times 10^{-4} \text{ M}$
  - $\text{K}^T = 6 \times 10^{-5} \text{ M}$
  - $\text{Na}^T = 2.8 \times 10^{-4} \text{ M}$
  - $\text{Fe(III)}^T = 5 \times 10^{-7} \text{ M}$
  - $\text{Cu}^T = 5 \times 10^{-8} \text{ M}$
  - $\text{Hg}^T = 10^{-9} \text{ M}$
  - $\text{Zn}^T = 1.5 \times 10^{-7} \text{ M}$
  - $\text{Ni}^T = 5 \times 10^{-9} \text{ M}$
  - $\text{Pb}^T = 10^{-9} \text{ M}$
  - $[\text{CO}_3]^T = 10^{-3} \text{ M}$
  - $[\text{SO}_4]^T = 10^{-4} \text{ M}$
  - $\text{Cl}^T = 2 \times 10^{-4} \text{ M}$

Titration of a model fresh water with cysteine

- Same concentrations as in previous EDTA figure
  - Except no Cu

Me: EDTA speciation

Me: Cysteine speciation

Metal speciation

Cysteine speciation

Figure 6.10 from: Morel & Hering, 1993

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-CO$_3$-citrate system
  - Best to use computer solution (MINEQL)

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**Surfactants**

- **Anionics**
  - 65%

- **Cationics**
  - 7%

- **Nonionics**
  - 28%

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

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
Chelators (builders) | Sodium tripolyphosphate, zeolite 4A, poly(acrylic acids)
Ion exchange | Sodium carbonate
Alkalies | Sodium carbonate, sodium tripolyphosphate, sodium citrate, sodium silicate
Bleaching agents | Sodium perborate, sodium nitrotriacetate (NTA)
Bleach activators | Tetraacetylene diamine
Bleach stabilizers | Ethylene diaminetetraacetae
Antiredeposition agents | Cellulose ethers
Enzymes | Proteases, amylases
Optical brighteners | Stilbene derivatives
Anticorrosion agents | Sodium silicate
Fabric softeners | Quaternary ammonium compounds
Dyes and blueing Agents | Sodium sulfate
Formulation aids | Quaternary ammonium salts
Fillers and water | Sodium sulfate

See: Knud-Hansen Paper

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 tripolyphosphate
Enzymes | Proteases
Optical brighteners | Stilbene derivatives
Anticorrosion agents | Triethanolamine
Fabric softeners | Sodium silicate, sodium silicate
Stabilizers | Triethanolamine
Fabric softeners | Quaternary ammonium salts
Fragrances | Sodium nitrotriacetate (NTA)
Dyes | Sodium nitrotriacetate (NTA)
Water |
To next lecture