Environmental Chemistry

# Metal speciation, complexation: solution

## 1) Complexometric titration

a) Calculate the total hardness of the sample using the following equations:

H (mol/L) = $\frac{V_L C_L}{V_0}$ = $\frac{2.6*0.05}{50}$ = 0.0025 M = 2.5 mM

Where $V_L$ = volume of EDTA solution used (mL)

$C_L$ = concentration of EDTA solution (M)

$V_0$ = volume of sample (mL)

The water is classified as intermediate.

b) Goal: formula for [M] as a function of known concentrations and constants.

We define: $H_2EDTA = H_2Y$ and $[Y]_{tot} = [Y]_{added}$

$K_1 = \frac{[HY^-][H^+]}{[H_2Y]} = 10^{-6.2}$ eq. 1

$K_2 = \frac{[Y^{2-}][H^+]}{[HY^-]} = 10^{-10.3}$ eq. 2

$[Y]_{tot} = [MY] + [Y] + [HY] + [H_2Y]$ eq. 3

Express [HY] and $[H_2Y]$ using eqs. 1 and 2 to get:

$[Y]_{tot} = [MY] + [Y](1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2})$

Introduce $(1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2}) = a_H$ and solve for [Y]:

$[Y] = \frac{[Y_{tot}] - [MY]}{a_H}$ eq.

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$[M]_{tot} = [MY] + [M]$

$[M] = [M]_{tot} - [MY]$ eq. 5

We do not have the concentration of [MY], we need to express it as a function of the total concentrations and available constants:

$K_{MY} = \frac{[MY]}{[Y][M]}$ eq. 6

Substitute [Y] (eq. 4) and [M] (eq. 5) in eq. 6 to get

$K_{MY} = \frac{[MY] a_H}{([M]_{tot} - [MY])([Y]_{tot} - [MY])}$

Re-structure to the form of a quadratic equation: $ax^2 + bx + c = 0$ with x = [MY]

$$[MY]^2 + [MY]([Y]_{tot} - [M]_{tot} - \frac{a_H}{K_{MY}}) + [Y]_{tot}[M]_{tot} = 0$$

Solve equation for [MY]: $x = \frac{-b + \pm\sqrt{b^2 - 4ac}}{2a}$

$$[MY] = \frac{[Y]_{tot} + [M]_{tot} + \frac{a_H}{K_{MY}} - \sqrt{([Y]_{tot} + [M]_{tot} + \frac{a_H}{K_{MY}})^2 - 4[Y]_{tot}([M]_{tot}}}{2} \qquad \text{eq. 7}$$

c) Calculate [MY] using eq. 7 above. pH 2 means $[H^+] = 10^{-2}$ M

For a successful complexometric titration, a high pH and high K are required (higher concentrations of [MY]).

| pH | [MY] | $logK_{MY}$ |
|---|---|---|
| 2 | 0 | 10 |
| 5 | $2.96\ 10^{-9}$ M | 10 |
| 7 | $6.21\ 10^{-7}$ M | 10 |
| 10 | $9.83\ 10^{-7}$ M | 10 |
| 5 | $4.32\ 10^{-11}$ M | 5 |
| 10 | $6.21\ 10^{-7}$ M | 10 |

## 2) Lead speciation

a) Speciation

$[Pb]_{tot} = [Pb^{2+}] + [PbOH^+] + [PbCO_3] = [Pb^{2+}](1 + 10^{6.3}\ [OH^-] + 10^{6.2}\ [CO_3^{2-}])$

$[CO_3^{2-}]_{tot} = [CO_3^{2-}] + [HCO_3^-]$

Thus, $[HCO_3^-] = [CO_3^{2-}]_{tot} - [CO_3^{2-}]$

$$K_a = 10^{-10.3} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = \frac{[CO_3^{2-}][H^+]}{[CO_3^{2-}]_{tot} - [CO_3^{2-}]}$$

$K_a[CO_3^{2-}]_{tot} - K_a[CO_3^{2-}] = [CO_3^{2-}][H^+]$

$$[CO_3^{2-}] = \frac{K_a[CO_3^{2-}]_{tot}}{K_a + [H^+]} = \frac{10^{-10.3}[CO_3^{2-}]_{tot}}{10^{-10.3} + 10^{-7.8}} = 4.1 * 10^{-6}\ M$$

Hence, $[Pb]_{tot} = [Pb^{2+}](1 + 1.26 + 6.50) = [Pb^{2+}] * 8.76$

<u>$[Pb^{2+}] = 1.14 * 10^{-10}$ M</u>

<u>$[PbOH^+] = 1.44 * 10^{-10}$ M</u>

$[Pb(CO_3)aq] = 7.41 * 10^{-10}$ M

b) Addition of EDTA

$[Y]_{tot} = [Y] + [HY] + [PbY] + [CaY]$

As PbY is a strong complex: $[PbY] \approx [Pb]_{tot} = 10^{-9}$ M

$[Y]_{tot} - [Pb]_{tot} = [Y] + [HY] + [CaY]$

Acid-base equilibrium: $\frac{[Y][H^+]}{[HY]} = 10^{-10.2}$

Complexation of $Ca^{2+}$: $\frac{[CaY]}{[Ca^{2+}][Y]} = 10^{10.7}$

$[Ca^{2+}]_{tot} = [Ca^{2+}] + [CaY]$

Since $[CaY] << [Ca^{2+}] \sim [Ca^{2+}]_{tot}$

$[Y]_{tot} - [Pb]_{tot} = [Y](1+ \frac{[H^+]}{10^{-10.2}}) + [CaY]$

$[Y]_{tot} - [Pb]_{tot} = [Y](1+ \frac{[H^+]}{10^{-10.2}}) + 10^{10.7}[Ca^{2+}]_{tot}[Y]$

$[Y]_{tot} - [Pb]_{tot} = [Y](1+ \frac{[H^+]}{10^{-10.2}} + 10^{10.7}[Ca^{2+}]_{tot})$

Solve for [Y] to get $[Y] = 1.98 * 10^{-15}$ M

$[Pb]_{tot} = [Pb^{2+}] (1 + 10^{6.3}[OH^-] + 10^{6.2}[CO_3^{2-}] + 10^{19.8}[Y])$

Solve for $[Pb^{2+}]$ to get $[Pb^{2+}] = 8 * 10^{-15}$ M

3) Hydrolysis of $Cu^{2+}$ and complex formation with $CO_3^{2-}$

$C_T = [H_2CO_3] + [HCO3-] + [CO_3^{2-}] + [CuCO_3] + 2 [Cu(CO_3)_2^{2-}]$

The last two terms can be neglected. Thus, we first calculate the $CO_3^{2-}$ concentration for pH = 8:

$C_T = [CO_3^{2-}](\frac{[H^+]^2}{K_{a1}K_{a2}} + \frac{[H^+]}{K_1} + 1)$

$[CO_3^{2-}] = 9.8 * 10^{-6}$ M

Now we can compute the individual Cu(II) species:

$[Cu]_T = [Cu^{2+}] + [CuOH^+] + [Cu(OH)_2] + [Cu(OH)_3^-] + [Cu(OH)_4^{2-}] + [CuCO_3] + [Cu(CO_3)_2^{2-}]$

$[Cu]_T = [Cu^{2+}](1 + {}^*ß_1[H^+]^{-1} + {}^*ß_2[H^+]^{-2} + {}^*ß_3[H^+]^{-3} + {}^*ß_4[H^+]^{-4} + {}^*ß_{1CO3}[CO_3^{2-}] + {}^*ß_{2CO3}[CO_3^{2-}]^2)$

For pH = 8.0, we obtain the following distribution

| **Species** | **Concentration (M)** | **% $Cu_T$** |
|---|---|---|
| $Cu^{2+}$ | $8.2 * 10^{-10}$ | 1.6 |
| $CuOH^+$ | $8.2 * 10^{-10}$ | 1.6 |
| $Cu(OH)_2$ | $5.2 * 10^{-10}$ | 1.0 |
| $Cu(OH)_3^-$ | $1.3 * 10^{-12}$ | $3 * 10^{-3}$ |
| $Cu(OH)_4^{2-}$ | $1 * 10^{-17}$ | $8 * 10^{-8}$ |
| $CuCO_3$ | $4.7 * 10^{-8}$ | 94.0 |
| $Cu(CO_3)_2^{2-}$ | $7.8 * 10^{-10}$ | 1.6 |