

Metal speciation, complexation

1) Complexometric titration

In class, we performed a complexometric titration to determine the water hardness of our sample. To this end, we titrated our sample with a strong ligand: ethylenediaminetetraacetic acid (EDTA).

a) Use the data that you have collected during the in-class experiment to calculate the total hardness of the water sample. Remember that the concentration of the EDTA solution used was 0.05 M. Is the water classified as soft, intermediate, or hard? Note that water with less than 2 mM of calcium carbonate is classified as soft, with 2-3 mM as intermediate, and with > 3 mM as hard.

b) There is a sharp change in the free metal concentration at the equivalence point, i.e., when equimolar addition of EDTA relative to the metal concentration is reached. Derive the general equation for the $[M]$ as a function of the added $[EDTA]$. Consider the speciation of M (free M and M -EDTA-complex) and H_2EDTA ($pK_1=6.2$, $pK_2=10.3$). The stability constant for M -EDTA-complex (K_{MY}) is $10^{14.3}$. Hint: use the mass balance equations for $[M]$ and $[EDTA]$ and solve for the M -EDTA-complex.

c) How is the titration affected by the pH (2-10) and the stability constants ($\log K$ 5 –10)? Calculate $[MY]$ for $[Y]_{tot}/[M]_{tot} = 1$ and $[M]_{tot} = 10^{-6}$ M for the following conditions. What conditions are critical for a complexometric titration?

$$\text{pH } 2, \log K_{MY} = 10$$

$$\text{pH } 5, \log K_{MY} = 10$$

$$\text{pH } 7, \log K_{MY} = 10$$

$$\text{pH } 7, \log K_{MY} = 5$$

$$\text{pH } 10, \log K_{MY} = 10$$

2) Lead speciation

Lead (Pb^{2+}) is present in a water with the following composition:

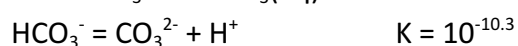
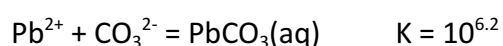
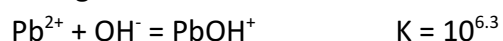
$$\text{pH } 7.8$$

$$[CO_3^{2-}]_{tot} = 1.3 \times 10^{-3} \text{ M}$$

$$[Pb^{2+}]_{tot} = 10^{-9} \text{ M}$$

$$[Ca^{2+}]_{tot} = 10^{-3} \text{ M}$$

The following constants are available:



a) Calculate the lead speciation for these conditions.

b) EDTA is added to the same water in a concentration of 10^{-7} M. How is the Pb(II) speciation affected?

Additional equilibria:



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

Estimate the equilibrium distribution of Cu(II) species in a carbonate-bearing water of pH =

8, $[\text{Cu(II)}]_{\text{tot}} = 5 \times 10^{-8}$ M and $C_{\text{tot}} = 2 \times 10^{-3}$ M. Use the following information.

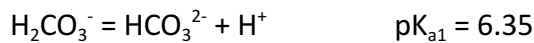


Tableau 6.2. Hydrolysis and CO_3^{2-} Complex Formation of Cu^{2+}

Components	Cu^{2+}	CO_3^{2-}	H^+	$\log K$ (25°C, I = 0)
Species Cu^{2+}	1	0	0	0
Cu(OH)^+	1	0	-1	-8.0
Cu(OH)_2^0	1	0	-2	-16.2
Cu(OH)_3^-	1	0	-3	-26.8
Cu(OH)_4^{2-}	1	0	-4	-39.9
CuCO_3^0	1	1	0	6.77
$\text{Cu(CO}_3)_2^{2-}$	1	2	0	10.01
H_2CO_3^*	0	1	2	16.6
HCO_3^-	0	1	1	10.3
CO_3^{2-}	0	1	0	0
OH^-	0	0	-1	-14
H^+	0	0	1	0
TOTCu²⁺ = 5×10^{-8} M $C_T = 2 \times 10^{-3}$ M pH given				