Lab 7
Experiment 22 (p.219)

Amino Acid Complexes: Stability constants of Ni(glycinate)$_n^{(2-n)^+}$
Acid-Base Chemistry of Glycine

Glycine is an example of a zwitterion.

What is a zwitterion?

A molecule that contains a (+) and (-) electrical charge at different location within the molecule.
What is the pH of this solution?

HNO$_3$ is a Strong Acid!

HNO$_3$ \( \rightarrow \) H$^+$ + NO$_3^-$

\[
[H^+] = [HNO_3] = 0.005 \text{ M}
\]

\[
pH = -\log(0.005) = 2.3
\]

How will the pH respond when glycinate is titrated into the solution?
Glycinate Titration

What is the pH of this solution?

HNO₃ is a Strong Acid!

\[ \text{HNO}_3 \rightarrow \text{H}^+ + \text{NO}_3^- \]

\[ [\text{H}^+] = [\text{HNO}_3] \]

\[ pH = -\log(0.005) = 2.3 \]

How will the pH respond when glycinate is titrated into the solution?
Glycinate Titration with Nickel

What is the pH of this solution?

0.1M KNO$_3$
5 mM HNO$_3$
5 mM Ni$^{2+}$

HNO$_3$ is a still a Strong Acid!

\[ [H^+] = [HNO_3] \]

\[ pH = -\log(0.005) = 2.3 \]

How will the pH response to glycinate titration differ with Ni$^{2+}$ in the solution?
Ni$^{2+}$-Glycinate Interactions

How will glycinate interact with Ni$^{2+}$?

MX$^+$

MX$_2$

MX$_3$
Ni$^{2+}$-Glycinate Interactions
Ni$^{2+}$-Glycinate Interactions

\[ \beta_1 = \frac{[MA^-]}{[M^{2+}][A^-]} \]
\[ \beta_2 = \frac{[MA_2^-]}{[M^{2+}][A^-]^2} \]
\[ \beta_3 = \frac{[MA_3^-]}{[M^{2+}][A^-]^3} \]
The Effect of Ni\(^{2+}\) on pH

Consider the simple glycine (HA) dissociation reaction:

\[ \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \]

\[ K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \]

\[ A_{\text{tot}} = [\text{A}^-] + [\text{HA}] \]

So why does Ni\(^{2+}\) influence this reaction?

Ni\(^{2+}\) preferentially binds to the base form (A\(^-\)) which alters the apparent \(K_a\) according to mass action (LeChatlier’s Principle)

\[ A_{\text{tot}} = [\text{A}^-] + [\text{HA}] + [\text{MA}^+] + [\text{MA}_2] + [\text{MA}_3^-] \]
Equilibrium Theory Approach

What we know…..

$M_{tot}$, $H_{tot}$ and $A_{tot}$ at any point in the titration

Glycinate is your titrant

$pH$ at any point in the titration

This is what you measure

$A_{tot} = [A^-] + [HA] + [MA^+] + [MA_2] + [MA_3^-]$

Equilibrium Expressions that describe these concentrations

$HA \rightleftharpoons H^+ + A^-$

$A^- + M^{2+} \rightleftharpoons MA^+$

$2A^- + M^{2+} \rightleftharpoons MA_2$

$3A^- + M^{2+} \rightleftharpoons MA_3^-$

$K_a = \frac{[H^+][A^-]}{[HA]} = 2.5 \times 10^{-10}$

$\beta_1 = \frac{[MA^-]}{[M^{2+}][A^-]}$

$\beta_2 = \frac{[MA_2]}{[M^{2+}]^2[A^-]}$

$\beta_3 = \frac{[MA_3^-]}{[M^{2+}][A^-]^3}$
Equilibrium Theory Approach

Fractional Saturation (ñ or θ)

The total number of ligands bound per metal ion

\[ A_{tot} = [A^-] + [HA] + [MA^+] + [MA_2] + [MA_3^-] \]

[Bound] =

[Metal] =

\[ \theta = \frac{[MA^-] + 2[MA_2] + 3[MA_3]}{M^{2+} + [MA^-] + [MA_2] + [MA_3]} \]

\[ \theta = \frac{\beta_1[A^-] + 2\beta_2[A^-]^2 + 3\beta_3[A^-]^3}{1 + \beta_1[A^-] + \beta_2[A^-]^2 + \beta_3[A^-]^3} \]
Equilibrium Theory Approach

Our goal is to cast $\theta$ in terms of known values

$$\theta = \frac{\beta_1 [A^-] + 2 \beta_2 [A^-]^2 + 3 \beta_3 [A^-]^3}{1 + \beta_1 [A^-] + \beta_2 [A^-]^2 + \beta_3 [A^-]^3}$$

$$[A^-] = \frac{K^a_{H^+}}{[H^+]} (C_H + [OH^-] - [H^+])$$

$C_H \rightarrow [H^+]$ from original HNO$_3$ solution

$$\theta = \frac{A_{tot} - \left(1 + \frac{K^a_{H^+}}{[H^+]}\right) (C_H + [OH^-] - [H^+])}{M_{tot}}$$
How are pKa values approximated from a pH titration?

\[ \text{pH @ } \frac{1}{2} \text{ Equivalence Point} \]

\[ pH = pK_a + \log \frac{[A^-]}{[HA]} \quad \text{pH} \]

\[ \theta = \frac{[HX]}{[X]_{tot}} \]
Graphical Approximation of $K_n$

\[ \log K_p - \frac{1}{2} = \frac{\theta}{2} \]

\[ pK_1 = -\log K_1 \]
\[ pK_2 = -\log K_2 \]
\[ pK_3 = -\log K_3 \]
Graphical Determination of $\beta_n$

$$\theta = \frac{\beta_1 [A^-] + 2 \beta_2 [A^-]^2 + 3 \beta_3 [A^-]^3}{1 + \beta_1 [A^-] + \beta_2 [A^-]^2 + \beta_3 [A^-]^3}$$

This expression can be rearranged to generate a less complex polynomial:

$$\frac{\theta}{(1 - \theta)[A^-]} = \frac{(3 - \theta)[A^-]^2}{(1 - \theta)} \beta_3 + \frac{(2 - \theta)[A^-]}{(1 - \theta)} \beta_2 + \beta_1$$

What happens at very low $[A^-]$?

$$\frac{\theta}{(1 - \theta)[A^-]} = \frac{(2 - \theta)[A^-]}{(1 - \theta)} \beta_2 + \beta_1$$
Graphical Determination of $\beta_n$

\[
\frac{\theta}{(1 - \theta)[A^-]} = \frac{(3 - \theta)[A^-]^2}{(1 - \theta)} \beta_3 + \frac{(2 - \theta)[A^-]}{(1 - \theta)} \beta_2 + \beta_1
\]

This expression can be further rearranged to generate a less complex polynomial:

\[
\frac{\theta - (1 - \theta)\beta_1[A^-]}{(2 - \theta)[A^-]} = \frac{(3 - \theta)[A^-]}{(2 - \theta)} \beta_3 + \beta_2
\]
Experimental Considerations

Prepare 200 mL of this solution

**Solid**

\[ \text{H}_2\text{NCHC} \rightarrow \text{H}_2\text{O} \rightarrow \text{pH} \sim 7 \text{ Glycinate} \]

0.4 M


***Nickel is a carcinogen! Ni salt will be massed in the fume hood***

Titrate glycinate into Ni solution in 0.2 mL increments.

Record pH for every aliquot.

……Hope you liked Chemometrics…..
How to start your spreadsheet

\[
\frac{\theta}{(1-\theta)[A^-]} = \frac{(3-\theta)[A^-]^2}{(1-\theta)} \beta_3 + \frac{(2-\theta)[A^-]}{(1-\theta)} \beta_2 + \beta_1
\]

What do you need to solve for \( \beta_n \)?

\[
[A^-] = \frac{K_a}{[H^+]} (C_H + [OH^-] - [H^+])
\]

\[
\theta = \frac{A_{tot} - \left(1 + \frac{K_a}{[H^+]}\right)(C_H + [OH^-] - [H^+])}{M_{tot}}
\]

Injection # | Volume | \( A_{tot} \) | pH | \([H^+]\) | \([OH^-]\) | \([A^-]\) | \( \theta \)
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