Zinc-EDTA Titration

You would like to perform a titration of 50.00 mL of a 1.00×10^{-4} M Zn^{2+} solution with a 1.00×10^{-4} M EDTA solution.

What is pZn at the equivalence point?

Log K_f for the ZnY^{2-} complex is 16.5.

Both solutions are buffered to a pH of 10.0 using a 0.100M ammonia buffer.

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Chem M3LC
Spring 2013

EDTA-Metal ion Complexation.

EDTA is a polyprotic acid - Ethylenediaminetetraacetic Acid. H_4Y.

$pK_1 = 1.99$; $pK_2 = 2.67$; $pK_3 = 6.16$; $pK_4 = 10.26$.

Alpha fraction for Y^{4-}:

$$\alpha_{Y^{4-}} = \frac{K_1K_2K_3K_4}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4}$$

$\alpha_{Y4-} = 0.355$ at pH =10.

We use an ammonia buffer solution for a reason...

Zinc Hydroxide

$$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_{2(s)}$$

Solubility product $K_{sp} = 3.0\times10^{-17}$

$$K_{sp} = [Zn^{2+}][OH^{-}]^2$$

At pH=10, $[Zn^{2+}]$ = ??

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At pH=10, $[Zn^{2+}] = K_{sp} / [OH^{-}]^2$

Zinc Hydroxide

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Solubility product $K_{sp} = 3.0\times10^{-17}$

$$K_{sp} = [Zn^{2+}][OH^{-}]^2$$

At pH=10, $[Zn^{2+}] = K_{sp}/[OH^{-}]^2$

$$= (3.0\times10^{-17})/(1.0\times10^{-4})^2$$

$$= 3.0\times10^{-9}\ M$$

This is the maximum free Zinc concentration.

Ammonia Buffer Solution

$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$ $pK_b = 4.74$

$[NH_3]_{total} = 0.100M$

At pH=10, $[NH_3]$ = ??

Ammonia Buffer Solution

$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$ $pK_b = 4.74$

$[NH_3]_{total} = 0.100M$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$[NH_3] = \alpha_{NH_3} C^{tot}$$

$$\alpha_{NH_3} = \left[1 + \frac{K_b}{[OH^-]}\right]^{-1}$$

At pH=10:

$[NH_3] = 0.0846\ M$

Zinc Complexation

Zinc - Ammonia Complexation

1. Zinc-ammonia complexation

$Zn^{2+} + NH_3 = Zn(NH_3)^{2+}$	$K_1 = 180$	$\beta_1 = K_1 = 180$
$Zn(NH_3)^{2+} + NH_3 = Zn(NH_3)_2^{2+}$	$K_2 = 220$	$\beta_2 = K_1K_2 = 3.96 \times 10^4$
$Zn(NH_3)_2^{2+} + NH_3 = Zn(NH_3)_3^{2+}$	$K_3 = 250$	$\beta_3 = K_1K_2K_3 = 9.90 \times 10^6$
$Zn(NH_3)_3^{2+} + NH_3 = Zn(NH_3)_4^{2+}$	$K_4 = 110$	$\beta_4 = K_1K_2K_3K_4 = 1.09 \times 10^9$

$$\alpha_{Zn^{2+}} = \frac{1}{1 + K_1[NH_3] + K_1K_2[NH_3]^2 + K_1K_2K_3[NH_3]^3 + K_1K_2K_3K_4[NH_3]^4}$$

At $[NH_3] = 0.0846M$, $\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$

Zinc - Ammonia Complexation

At a TOTAL Zinc concentration of 1.00×10^{-4} M:

$$[Zn^{2+}] = \alpha_{Zn^{2+}} [Zn^{2+}]^{tot}$$

$$[Zn^{2+}] = (1.61 \times 10^{-5})(1.00 \times 10^{-4})$$

$$[Zn^{2+}] = 1.61 \times 10^{-9}\ M$$

Therefore: no precipitation!

Once more, with feeling:

EDTA Titration

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What is pZn at the equivalence point?

Log Kf for the ZnY^{2-} complex is 16.5.
Both solutions are buffered to a pH of 10.0 using a 0.100M ammonia buffer.

The alpha fraction for Y^{4-} is 0.355 at a pH of 10.0.
The alpha fraction for Zn^{2+} is 1.61×10^{-5}.

EDTA Titration

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Total moles of Zinc = ??

EDTA Titration

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Total moles of Zinc $= (1.00 \times 10^{-4}\ \text{M})(0.050\text{L})$

$= 5.0 \times 10^{-6}$ moles

EDTA Titration

You would like to perform a titration of 50.00 mL of a 1.00×10^{-4} M Zn^{2+} solution with a 1.00×10^{-4} M EDTA solution.

Total moles of Zinc = 5.0×10^{-6} moles

Equivalence point volume = ??

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Equivalence point volume = 0.100L

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Equivalence point volume = 0.100L

$[ZnY^{2-}]$ = ??

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Total moles of Zinc = 5.0×10^{-6} moles

Equivalence point volume = 0.100L

$[ZnY^{2-}]$ = 5.0×10^{-5} M

We assume a stoichiometric reaction.

EDTA Titration

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Total moles of Zinc = 5.0×10^{-6} moles

Equivalence point volume = 0.100L

$[ZnY^{2-}] = 5.0 \times 10^{-5}$ M

$[Zn^{2+}]$ = ??

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$[ZnY^{2-}] = 5.0 \times 10^{-5}$ M

We assumed a stoichiometric reaction. But actually, there is a little bit of free (uncomplexed) EDTA and free (uncomplexed) Zinc in solution.

$$[Zn^{2+}] = \alpha_{Zn^{2+}} C^{Total}_{Free\ Zn}$$

$$[Y^{4-}] = \alpha_{Y^{4-}} C^{Total}_{Free\ EDTA}$$

$$C^{Total}_{Free\ Zn} = C^{Total}_{Free\ EDTA}$$

$$C^{Total}_{Free\ Zn} = \sqrt{\frac{[ZnY^{2-}]}{\alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f}}$$

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$[ZnY^{2-}] = 5.0 \times 10^{-5}$ M

We assumed a stoichiometric reaction. But actually, there is a little bit of free (uncomplexed) EDTA and free (uncomplexed) Zinc in solution.

$$[Zn^{2+}] = \alpha_{Zn^{2+}} C_{Free\ Zn}^{Total}$$

$$[Y^{4-}] = \alpha_{Y^{4-}} C_{Free\ EDTA}^{Total}$$

$$C_{Free\ Zn}^{Total} = C_{Free\ EDTA}^{Total}$$

$$C_{Free\ Zn}^{Total} = \sqrt{\frac{[ZnY^{2-}]}{\alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f}}$$

Log Kf = 16.5.

$\alpha_{Y4-} = 0.355$

$\alpha_{Zn2+} = 1.61 \times 10^{-5}$

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$[ZnY^{2-}] = 5.0 \times 10^{-5}$ M

We assumed a stoichiometric reaction. But actually, there is a little bit of free (uncomplexed) EDTA and free (uncomplexed) Zinc in solution.

$$[Zn^{2+}] = \alpha_{Zn^{2+}} C^{Total}_{Free\ Zn}$$

$$[Y^{4-}] = \alpha_{Y^{4-}} C^{Total}_{Free\ EDTA}$$

$$C^{Total}_{Free\ Zn} = C^{Total}_{Free\ EDTA}$$

$$C^{Total}_{Free\ Zn} = \sqrt{\frac{[ZnY^{2-}]}{\alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f}}$$

$$C^{Total}_{Free\ Zn} = 1.66 \times 10^{-8} \text{ M}$$

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Total moles of zinc = 5.0×10^{-6} moles

Equivalence point volume = 0.100L

$[ZnY^{2-}]$ = 5.0×10^{-5} M

$C_{Free\ Zn}^{Total}$ = 1.66×10^{-8} M

$$[Zn^{2+}] = \alpha_{Zn^{2+}} C_{Free\ Zn}^{Total}$$

EDTA Titration

You would like to perform a titration of 50.00 mL of a 1.00×10^{-4} M Zn^{2+} solution with a 1.00×10^{-4} M EDTA solution.

Total moles of zinc = 5.0×10^{-6} moles

Equivalence point volume = 0.100L

$[ZnY^{2-}] = 5.0 \times 10^{-5}$ M

$C^{Total}_{Free\ Zn} = 2.35 \times 10^{-6}$ M

$[Zn^{2+}] = \alpha_{Zn^{2+}} C^{Total}_{Free\ Zn} = (1.61 \times 10^{-5})(1.66 \times 10^{-8}\ M)$

$[Zn^{2+}] = 2.59 \times 10^{-13}$ M

pZn = 12.6

We are done!