1) A 40.0 ML Solution Of 0.0350M Piperidine (pKa =11.13) Is Titrated With 0.0650MHCl. Calculate The PH

1) A 40.0 ML Solution Of 0.0350M Piperidine (pKa =11.13) Is Titrated With 0.0650MHCl. Calculate The PH

Understanding how to determine the pH during titrations involving weak bases such as piperidine is fundamental in analytical chemistry. This problem provides a scenario where a known volume and concentration of piperidine are titrated with a strong acid, hydrochloric acid (HCl). The goal is to calculate the pH at a particular point in the titration process, which requires applying principles of acid-base chemistry, equilibrium calculations, and stoichiometry.

In this article, we will explore the step-by-step methodology to determine the pH of the solution during the titration process, emphasizing the concepts of weak base dissociation, buffer solutions, equivalence point, and the use of pKa values. Additionally, we will discuss relevant concepts such as the relationship between pKa and pKb, the calculation of initial pH, the titration curve, and the pH at various stages of titration.

Understanding the Components of the Titration

1. Piperidine as a Weak Base

Piperidine is a cyclic secondary amine with the molecular formula C5H11N. Its behavior in aqueous solution is characterized by its ability to accept protons, making it a weak base. The pKa value given (pKa = 11.13) refers to the conjugate acid of piperidine, which is protonated piperidine (piperidinium ion).

The key relationships are:
- pKa of conjugate acid = 11.13
- pKb of piperidine = 14 – pKa = 2.87

Understanding these relationships is crucial for analyzing the solution's behavior during titration.

2. Hydrochloric Acid as a Strong Acid

HCl is a strong acid that dissociates completely in aqueous solution:
$$\mathrm{HCl} \rightarrow \mathrm{H^+} + \mathrm{Cl^-}$$

When titrated with a weak base like piperidine, the HCl provides protons (H+) that react with the base to form its conjugate acid (piperidinium ion).

Initial Solution: Calculating the Starting pH

Before titration begins, the initial pH of the piperidine solution must be established. This involves calculating the equilibrium concentration of hydroxide ions (OH-) in the solution based on its initial concentration and pKa.

1. Initial Concentration of Piperidine

Given:
- Volume of piperidine solution = 40.0 mL = 0.0400 L
- Concentration of piperidine = 0.0350 M

The initial moles of piperidine:

$$ n_{base} = C \times V = 0.0350\, \mathrm{mol/L} \times 0.0400\, \mathrm{L} = 1.4 \times 10^{-3}\, \mathrm{mol} $$

2. Calculating the Initial pOH and pH

Since piperidine is a weak base, it partially ionizes:

$$ \mathrm{Pip} + \mathrm{H_2O} \rightleftharpoons \mathrm{PipH^+} + \mathrm{OH^-} $$

The equilibrium expression:

$$ K_b = \frac{[\mathrm{PipH^+}][\mathrm{OH^-}]}{[\mathrm{Pip}]} $$

Using the relation:

$$ pK_a + pK_b = 14 $$

$$ pK_b = 14 - pK_a = 14 - 11.13 = 2.87 $$

Calculate K_b:

$$ K_b = 10^{-pK_b} = 10^{-2.87} \approx 1.35 \times 10^{-3} $$

Set up the ICE table for initial dissociation:
- Initial concentration: 0.0350 M
- Change: Let x be the concentration of OH- at equilibrium

$$ K_b = \frac{x^2}{0.0350 - x} $$

Assuming $x \ll 0.0350$:

$$ K_b \approx \frac{x^2}{0.0350} \Rightarrow x^2 = K_b \times 0.0350 $$

$$ x^2 = 1.35 \times 10^{-3} \times 0.0350 \approx 4.725 \times 10^{-5} $$

$$ x \approx \sqrt{4.725 \times 10^{-5}} \approx 6.87 \times 10^{-3} \, \mathrm{M} $$

Thus:
- $[\mathrm{OH^-}] \approx 6.87 \times 10^{-3}\, \mathrm{M}$

Calculate pOH:
$$ pOH = -\log[\mathrm{OH^-}] = -\log(6.87 \times 10^{-3}) \approx 2.16 $$

Finally, calculate pH:
$$ pH = 14 - pOH = 14 - 2.16 = 11.84 $$

Initial pH of the piperidine solution is approximately 11.84.

Progression of Titration and pH Calculation at Various Stages

The titration process involves adding HCl gradually to the piperidine solution. The pH at any point depends on the amount of acid added, the initial amount of base, and the extent of neutralization.

1. Calculating the Volume of HCl Needed to Reach Different Points

- At the start: No HCl added; pH ≈ 11.84
- At the equivalence point: When moles of HCl added equal moles of piperidine
- Beyond the equivalence point: Excess HCl determines the pH

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2. Moles of HCl Needed to Reach Equivalence Point

Given:
- Concentration HCl = 0.0650 M
- Moles of piperidine = 1.4 × 10-3 mol

Moles of HCl required:
$$ n_{HCl} = n_{piperidine} = 1.4 \times 10^{-3}\, \mathrm{mol} $$

Volume of HCl needed:
$$ V_{HCl} = \frac{n_{HCl}}{C_{HCl}} = \frac{1.4 \times 10^{-3}}{0.0650} \approx 0.0215\, \mathrm{L} = 21.5\, \mathrm{mL} $$

At 21.5 mL of HCl added, the solution is at the equivalence point.

Calculating pH at the Equivalence Point

At the equivalence point, all piperidine has been converted to its conjugate acid (piperidinium ion). The pH depends on the hydrolysis of this conjugate acid.

Key steps:

- Find the concentration of the conjugate acid
- Determine the hydrolysis equilibrium
- Calculate the pH from the hydrolysis constant

1. Moles of conjugate acid formed:

Since initial moles of piperidine = 1.4 × 10-3 mol, at the equivalence point, this is the amount of piperidinium ion.

Total volume after titration:
\[V_{total} = 40.0\, \mathrm{mL} + 21.5\, \mathrm{mL} = 61.5\, \mathrm{mL} = 0.0615\, \mathrm{L} \]

Concentration of piperidinium:
\[[\mathrm{PipH^+}] = \frac{1.4 \times 10^{-3}}{0.0615} \approx 0.0228\, \mathrm{M} \]

- The hydrolysis of piperidinium:
\[\mathrm{PipH^+} + \mathrm{H_2O} \rightlefttharpoons \mathrm{Pip} + \mathrm{H_3O^+} \]

Hydrolysis constant:
\[K_a = 10^{-pK_a} = 10^{-11.13} \approx 7.41 \times 10^{-12} \]

- The conjugate acid hydrolyzes slightly, producing H+ ions, which determine the pH.

Set up hydrolysis equilibrium:
\[K_{hyd} = \frac{[\mathrm{Pip}][\mathrm{H_3O^+}]}{[\mathrm{PipH^+}]} \approx K_a \]

Assuming:
- \([\mathrm{H_3O^+}] = x\)
- \([\mathrm{Pip}] = x\)

Then:
\[K_a = \frac{x^2}{[\mathrm

Frequently Asked Questions

What is the initial pH of the 0.0350 M piperidine solution before titration?

The initial pH can be calculated using the pKa of piperidine and its concentration. pH = 14 - pKa + log [base] = 14 - 11.13 + log 0.0350 ≈ 2.87.

How do you determine the amount of HCl needed to reach the equivalence point in this titration?

The moles of piperidine are 0.0400 L × 0.0350 mol/L = 0.0014 mol. Since HCl reacts 1:1, the HCl required is 0.0014 mol. Using the concentration of HCl (0.0650 M), the volume needed is 0.0014 mol / 0.0650 mol/L ≈ 0.0215 L or 21.5 mL.

What is the pH at the equivalence point for this titration?

At the equivalence point, the solution contains the conjugate acid of piperidine, which is a weak acid. The pH can be found using the hydrolysis of the conjugate acid, but typically, for a weak base-strong acid titration, the pH at equivalence is less than 7, approximately around 5.3 to 5.5.

How do you calculate the pH after adding 10 mL of HCl during titration?

Adding 10 mL of 0.0650 M HCl introduces 0.00065 mol of HCl. The remaining moles of piperidine are 0.0014 mol - 0.00065 mol = 0.00075 mol. The total volume is 40 mL + 10 mL = 50 mL or 0.050 L. The new concentrations are piperidine: 0.00075 mol / 0.050 L = 0.015 mol/L, and HCl: 0.00065 mol / 0.050 L = 0.013 mol/L. Since piperidine is in excess, the solution is still basic, and pH can be calculated based on the remaining base.

What is the significance of the pKa value in calculating the pH of the solution?

The pKa value indicates the strength of the conjugate acid/base system. It helps determine the pH of the solution at different stages of titration, especially when calculating the pH of weak base or weak acid solutions and at the equivalence point.

How does the pKa of piperidine influence the shape of the titration curve?

Since piperidine has a pKa of 11.13, its conjugate acid is relatively weak, resulting in a titration curve that shows a gradual pH increase until near the equivalence point, where a sharp rise occurs. The high pKa means the base is strong enough to maintain a high pH until close to neutralization.

Additional Resources

Titration: Unlocking the pH Dynamics of Piperidine with Hydrochloric Acid

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Introduction

In the realm of analytical chemistry, titrations serve as fundamental techniques for quantifying the concentration of unknown solutions, understanding acid-base equilibria, and exploring the intricate behaviors of organic compounds. Among the numerous titrants and analytes studied, the titration of amines such as piperidine with strong acids like hydrochloric acid (HCl) offers insights into their basicity, buffer capacities, and pKa values. This detailed examination aims to compute the pH of a 40.0 mL solution of 0.0350 M piperidine during its titration with 0.0650 M HCl, providing a comprehensive understanding of the underlying chemistry involved.

Background: Piperidine and Its Basicity

Piperidine is a saturated heterocyclic amine with the molecular formula $C_5H_{11}N$. Its structure resembles that of a cyclopentane ring with a nitrogen atom replacing one carbon atom. As a secondary amine, piperidine exhibits basic behavior, meaning it readily accepts protons. Its pKa value, 11.13, reflects its tendency to accept a proton in aqueous solution — a higher pKa indicates a stronger base among amines.

This property plays a pivotal role in titration calculations, especially when determining the pH at various stages of neutralization, whether in the initial solution, during the equivalence point, or in the buffer regions.

Understanding the Titration Setup

To analyze the titration process, consider the following parameters:

- Initial volume of piperidine solution (V_1): 40.0 mL (or 0.0400 L)
- Concentration of piperidine (C_1): 0.0350 M
- Concentration of HCl titrant (C_2): 0.0650 M

The goal is to compute the pH of the solution at a specific point during titration — specifically, before any HCl has been added — and then explore how the pH evolves as titrant is added, focusing on the initial stage.

Step 1: Calculating Initial pH (Before Titration)

Before titrant addition, the solution contains only piperidine, a weak base. Its initial pH can be determined using the base dissociation equilibrium:

$$ \text{Piperidine} + \text{H}_2\text{O} \leftrightarrow \text{PiperidineH}^+ + \text{OH}^- $$

The equilibrium expression is governed by the base dissociation constant K_b:

$$ K_b = \frac{K_w}{K_a} $$

Where:

- K_w = 1.0×10^{-14} (ionization constant of water)
- K_a = $10^{-\text{p}K_a} = 10^{-11.13}$

Calculating K_b:

$$
K_b = \frac{1.0 \times 10^{-14}}{10^{-11.13}} = 10^{-(14 - 11.13)} = 10^{-2.87} \approx 1.35 \times 10^{-3}
$$

Step 2: Determining the Initial Concentration of Piperidine

$$ C_{initial} = 0.0350\, \text{M} $$
$$ V_{initial} = 40.0\, \text{mL} = 0.0400\, \text{L} $$

Number of moles of piperidine:

$$
n_{piperidine} = C_{initial} \times V_{initial} = 0.0350\, \text{mol/L} \times 0.0400\, \text{L} = 1.40 \times 10^{-3}\, \text{mol}
$$

Step 3: Calculating Initial pOH and pH

Using the K_b expression:

$$
K_b = \frac{[OH^-]^2}{[Piperidine]_{initial} - [OH^-]} \approx \frac{[OH^-]^2}{[Piperidine]_{initial}}
$$

Assuming $x = [OH^-]$ is small relative to initial concentration:

$$
x^2 = K_b \times [Piperidine]_{initial}
$$

$$
x^2 = 1.35 \times 10^{-3} \times 0.0350\, \text{M} = 4.725 \times 10^{-5}

\]

$$
x = \sqrt{4.725 \times 10^{-5}} \approx 6.87 \times 10^{-3}\, \text{M}
$$

pOH is:

$$
pOH = -\log [OH^-] = -\log (6.87 \times 10^{-3}) \approx 2.16
$$

Therefore, the initial pH:

$$
pH = 14 - pOH = 14 - 2.16 = 11.84
$$

Initial pH ≈ 11.84

This high pH confirms piperidine's strong basic nature.

Step 4: Titration Progress — Adding HCl

As HCl is added, it reacts with piperidine:

$$
\text{Piperidine} + \text{HCl} \rightarrow \text{Piperidinium chloride} \quad (\text{a salt})
$$

The reaction consumes base, decreasing pH. To determine the pH at any point, particularly early in the titration (before the equivalence point), we analyze the remaining base and the formed salt.

Step 5: Calculating the pH After Partial Neutralization

Suppose a volume V_{HCl} of 0.0650 M HCl has been added. The moles of HCl added:

$$
n_{HCl} = C_{HCl} \times V_{HCl}
$$

The moles of piperidine remaining:

$$
n_{piperidine, remaining} = n_{piperidine, initial} - n_{HCl}
$$

The solution contains a mixture of unreacted piperidine and its conjugate acid (piperidinium). Since pKa is known, and the solution is a buffer during the titration, the pH can be calculated using the Henderson-Hasselbalch equation:

\[
pH = pK_a + \log \left(\frac{[\text{Base}]}{[\text{Acid}]} \right)
\]

Where:

- \([\text{Base}]\) = moles of unreacted piperidine divided by the total volume
- \([\text{Acid}]\) = moles of piperidinium chloride formed divided by the total volume

---

Step 6: Example Calculation at a Specific Point

Let's assume 10.0 mL of HCl has been added:

\[
V_{HCl} = 10.0\, \text{mL} = 0.0100\, \text{L}
\]

Number of moles of HCl:

\[
n_{HCl} = 0.0650\, \text{mol/L} \times 0.0100\, \text{L} = 6.50 \times 10^{-4}\, \text{mol}
\]

Remaining piperidine:

\[
n_{piperidine, remaining} = 1.40 \times 10^{-3} - 6.50 \times 10^{-4} = 7.50 \times 10^{-4}\, \text{mol}
\]

Formed piperidinium:

\[
n_{piperidinium} = 6.50 \times 10^{-4}\, \text{mol}
\]

Total volume:

\[
V_{total} = 40.0\, \text{mL} + 10.0\, \text{mL} = 50.0\, \text{mL} = 0.0500\, \text{L}
\]

Concentrations:

\[

$$
[\text{Base}] = \frac{7.50 \times 10^{-4}}{0.0500\, \text{L}} = 0.0150\, \text{M}
$$

$$
[\text{Acid}] = \frac{6.50 \times 10^{-4}}{0.0500\, \text{L}} = 0.0130\, \text{M}
$$

Applying Henderson-Hasselbalch:

$$
pH = 11.13 + \log \left(\frac{0.0150}{0.0130} \right) \approx 11.13 + \log(1.154) \approx 11.13 + 0.062 \approx 11.19
$$

pH after adding 10 mL of HCl is approximately 11.19.

Additional Considerations

- At the Equivalence Point: When moles of HCl added equal initial moles of piperidine, the solution contains only piperidinium chloride

1 A 40 0 Ml Solution Of 0 0350m Piperidine Pka 11 13 Is Titrated With 0 0650mhcl Calculate The Ph

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