Acid-Base Properties and Solubility

Background

The relative acidity of organic molecules plays a large role in their reactivity and physical properties. Knowledge of pKₐs is critical for predicting acid-base reactions and understanding extractions in organic chemistry lab.

In aqueous solution, an acid reacts with water to form hydronium ion (H₃O⁺) and its conjugate base, known as acid hydrolysis. A base reacts with water to form hydroxide (OH⁻) and its conjugate acid, known as base hydrolysis.

\[
\text{Acid Hydrolysis: \quad HA + H₂O \rightleftharpoons H₃O⁺ + A⁻} \\
\text{Base Hydrolysis: \quad B + H₂O \rightleftharpoons OH⁻ + \text{BH}⁺}
\]

Strong acids have conjugate bases (A⁻) that stabilize negative charges – the more stable the conjugate base, the more the equilibrium gets pushed to the right. The pH scale is based on hydronium concentration, and the more hydronium, the more acidic the solution and the lower the pH. If the conjugate base has resonance, it helps to stabilize the negative charge thus resulting in a stronger acid. For instance, carboxylic acids are more acidic than alcohols because their conjugate bases are resonance stabilized. Electron withdrawing groups will also stabilize a negative charge

\[
\begin{align*}
\text{COOH} & + H₂O \rightleftharpoons H₃O⁺ + [\text{COO}^-] \\
\text{HOH} & + H₂O \rightleftharpoons H₃O⁺ + \text{O}⁻
\end{align*}
\]

In aqueous solution, bases produce hydroxide, which lowers the hydronium concentration and raises the pH. All bases have lone pairs. If a lone pair is involved in resonance it decreases the basicity because protonation interrupts those stabilizations. For instance, when propanamide is protonated, the nitrogen lone pair can no longer be in resonance with the carbonyl. Propylamine had no resonance to begin with, so when it is protonated, nothing is lost and it is therefore considerably more basic than propanamide.

\[
\begin{align*}
\text{propanamide} & \quad + H₂O \rightleftharpoons \text{OH⁻} + \text{CH₃CH(NH₂)CH₂OH} \\
\text{propylamine} & \quad + H₂O \rightleftharpoons \text{OH⁻} + \text{CH₃CH₂N(CH₃)₂}
\end{align*}
\]

The acid-base properties of organic molecules also affects their aqueous solubility. Generally only small or highly polar organic molecules are soluble in neutral water. However, if an acid-base reaction converts an organic compound to an ion, it will become water soluble. For example, phenol is only slightly water soluble at room temperature. If mixed with a strong enough base it forms its conjugate base which is ionic. Therefore phenol is slightly soluble in neutral water but highly soluble in aqueous sodium hydroxide. The solubility can be reversed by neutralizing the hydroxide solution.

\[
\text{phenol} + \text{Na⁺OH⁻} \rightleftharpoons \text{H₂O} + \text{C₆H₅O⁻Na⁺}
\]
**Like dissolves like.** The basic principle of solubility is that molecules with similar intermolecular forces (IMFs) will solvate each other, molecules with dissimilar forces will not. If two liquids dissolve in each other they are said to *miscible*. Oil and water are immiscible because they have different dominant IMFs.

**Procedure**

**Part I – pH of Ethanol/Water solutions**

50% ethanol solutions of benzenesulfonic acid, benzoic acid, benzylamine, p-cresol, and p-toluidine will be prepared ahead of time. Obtain a well plate and transfer 5 drops of each solution into the separate wells and 2 drops of universal indicator solution into each well. Determine the relative acidity or basicity of the compounds based on the color of the solution.

![Chemical structures](image)

- benzenesulfonic acid
- benzoic acid
- benzylamine
- p-cresol
- p-toluidine

**Part II – Solubility and pH**

Obtain 3 clean test tubes and place approximately 0.04 g benzoic acid in each. Add 2 mL of water to test tube 1, 2 mL of 1.5 M NaOH to test tube 2, and 1.5 M HCl to test tube 3. Shake gently and observe solubility of each. Next, add 3 mL of 1.5 M HCl to test tube 2 and observe.

**Part III – Solubility of solids**

Obtain 4 test tubes. Place 0.04 g of solid and 1 mL of liquid in the test tubes according to the table below. Shake the test tube for 20 seconds and observe solubility.

| test tube 1 | biphenyl | water |
| test tube 2 | biphenyl | hexane |
| test tube 3 | succinic acid | water |
| test tube 4 | succinic acid | hexane |

**Part IV – Miscibility of liquids**

Obtain 5 test tubes. Mix the together the 1 mL of each of the following and observe if they are miscible or not. Shake the test tube for 20 seconds and observe if two layers form upon settling.

| test tube 1 | water | ethanol |
| test tube 2 | water | benzyl alcohol |
| test tube 3 | water | hexane |
| test tube 4 | water | ethyl ether |
| test tube 5 | hexane | ethyl ether |

**Chemicals:** 50% ethanol, benzenesulfonic acid, benzoic acid, benzylamine, p-cresol, p-toluidine, HCl (aq), NaOH (aq), ethanol, benzyl alcohol, hexane, ethyl ether, biphenyl, succinic acid