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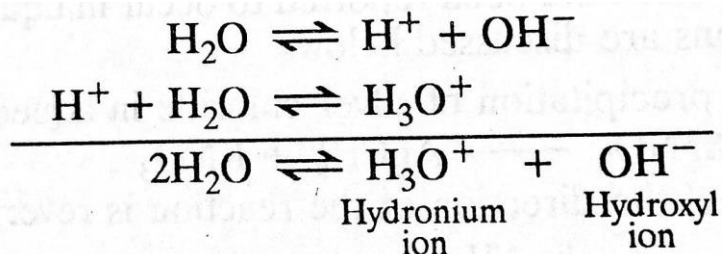
**TOPIC: - Non aqueous solvent  
Protic solvent, Liquid ammonia**

## **Protic solvents**

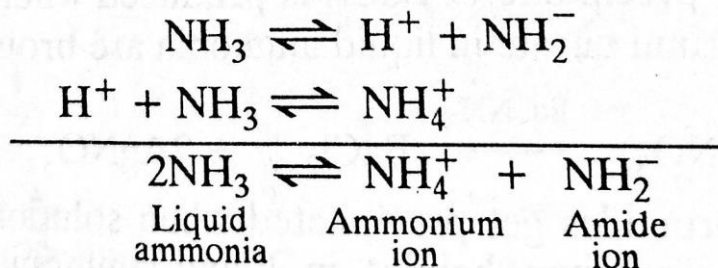
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### **Introduction**

This section considers solvent properties of some protic solvents including liquid ammonia, acetic acid anhydrous tetraoxosulphate (VI) acid and hydrogen fluoride. The commonest feature of these solvents is their ability to produce proton, which implies that they are aligned to Bronsted-Lowry acid and base. For example, they undergoes self-ionization according to the following equation,



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$



The self-ionization equation reveals that these solvents can behave as an acid or base depending on the proton affinity of the substance that they solvate. For example, any substance that will produced protons ( $\text{H}^+$ ), in liquid ammonia, acetic acid, anhydrous sulphuric acid and hydrogen fluoride will be an acid respectively. Similarly if any substance that has strong affinity for proton in liquid ammonia, acetic acid, anhydrous sulphuric acid and hydrogen fluoride respectively will be regarded as a base. Among these solvents, liquid ammonia seems to be more universal than others. Therefore much reaction details are available for liquid ammonia than acetic

acid, anhydrous tetraoxosulphate (VI) acid and hydrogelfouride. Brief introduction is also provided for superacids solvents.

### **Objectives**

- i. To know physical properties of liquid ammonia, acetic acid and anhydrous sulphuric acid that enhances its solvent properties
- ii. To study autoionization property of liquid ammonia, acetic acid and anhydrous sulphuric acid
- iii. To compare the autoionization property of liquid ammonia, acetic acid and anhydrous sulphuric acid with each other and with aqueous medium.
- iv. To study and comprehends the various reactions that are carried out in liquid ammonia, acetic acid and anhydrous sulphuric acid
- v. To compare the solvent behaviours of ammonia, acetic acid and anhydrous sulphuric acid with that of water
- vi. To introduce super acids and hydrogen fluoride as solvents

## **Main content**

### **Liquid ammonia**

Liquid ammonia is a widely used nonaqueous solvent. At atmospheric pressure, ammonia ( $\text{NH}_3$ ), is present as a liquid at temperatures below  $-33.6\text{ }^\circ\text{C}$  ( $-28.5\text{ }^\circ\text{F}$ ). At 10 bar, the condensation/boiling point is  $25\text{ }^\circ\text{C}$  ( $77\text{ }^\circ\text{F}$ ). The melting and boiling points of liquid  $\text{NH}_3$  are lower than those of water while its liquid range is  $-77$  to  $-33$ , which make it difficult for handling. Just like in water, liquid  $\text{NH}_3$  also shows hydrogen bonding but  $\text{NH}_3$  molecules are less strongly associated because nitrogen is less electronegative than oxygen. Therefore, the freezing point and boiling point of ammonia are less. The dielectric constant of liquid ammonia (22 at  $-33$ ) is lower than that of water (78.5 at  $25$ ). Therefore, liquid ammonia is expected to be a poor solvent for ionic compounds. However, the solvent has lower viscosity (0.254 cp at  $-33$ ) than water (0.959 cp at  $25$ ). Consequently, liquid ammonia exhibits greater ionic mobility and thereby compensates to some extent for the effect of dielectric constant.

### **Solved problem 1**

Give reasons for the following solvent property of liquid ammonia

- i. liquid ammonia exhibit greater ionic mobility
- ii. Liquid ammonia is difficult for handling
- iii. Liquid ammonia is expected to be a poor solvent for polar substances compared to water.
- iv. Hydrogen bond is weaker in liquid ammonia than in water

### **Solution**

- i. Liquid ammonia has lower viscosity than water
- ii. The liquid range of liquid ammonia is  $-77$  to  $-33^{\circ}\text{C}$
- iii. The dielectric constant of liquid ammonia (22 at  $-33^{\circ}\text{C}$ ) is lower than that of water (78.5 at  $25^{\circ}\text{C}$ ).
- iv. Nitrogen is less electronegative than oxygen