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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, aceticacid 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,

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$H^+ + H_2O \rightleftharpoons H_3O^+$$
$$2H_2O \rightleftharpoons \underset{\text{Hydronium ion}}{H_3O^+} + \underset{\text{Hydroxyl ion}}{OH^-}$$

$$K_w = [H_3O^+][OH^-] = 1{\cdot}0\times10^{-14} \text{ at } 25°C$$

$$NH_3 \rightleftharpoons H^+ + NH_2^-$$
$$H^+ + NH_3 \rightleftharpoons NH_4^+$$
$$2NH_3 \rightleftharpoons \underset{\text{Liquid ammonia}}{NH_4^+} + \underset{\text{Ammonium ion}}{NH_2^-} \quad \underset{\text{Amide ion}}{}$$

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 (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 hydrogeflouride. 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 use nonaqueous solvent. At atmospheric pressure, ammonia(NH3), is present as aliquid at temperatures below -33.6 °C (-28.5 °F). At 10 bar, the condensation/boiling point is 25 °C (77 °F) The melting and boiling points of liquid NH3 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 NH3 also show hydrogen bonding but NH3 molecules are less strongly associated because nitrogen is less electronegative than oxygen. Therefore 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 forionic compounds. However, the solvent has lower viscosity (0.254cp at -33) than water (0.959cp at 25).. Consequently, liquid ammonia exhibit greater ionic mobility and thereby compensate 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
iii. The dielectric constant of liquid ammonia (22 at -33) is lower than that of water (78.5 at 25).
iv. Nitrogen is less electronegative than oxygen