E-Content Study Material

B. Sc. Chemistry (H)

2^{nd} Year

Paper II B

Inorganic Chemistry

Chapter VIII: Non-aqueous Solvents

Topic: Reactions in Liquid NH_3

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Liquid Ammonia

Liquid ammonia is one of the most extensively studied non-aqueous solvents. It is a protonic solvent and its water-like properties have made it a highly useful solvent and a reaction medium for carrying out several types of organic and inorganic reactions. Liquid ammonia shows a striking resemblance with water in its solvent action. Ammonia molecules are, however less strongly associated through hydrogen bonding in liquid ammonia. Consequently, the freezing and boiling points of liquid ammonia are lower than those of water. Another similarity with water is the polarity of the ammonia molecule. It has a pyramidal structure which makes it polar. A third similarity is autoionisation of liquid ammonia, similar to the autoionisation of water. Both liquid ammonia and water show comparable autoionisation, represented as below:

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$H^+ + H_2O \rightleftharpoons H_3O^+$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Hydronium ion Hydroxyl ion

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^oC$$

$$NH_3 \rightleftharpoons H^+ + NH_2^-$$

$$H^+ + NH_3 \rightleftharpoons NH_4^+$$

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

Liquid ammonia Ammonium ion Amide ion

$$K_b = [NH_4^+][NH_2^-] = 1.9 \times 10^{-33} \text{ at } -50^oC.$$

However, the extent of autoionisation of liquid ammonia is much less than that of water (compare the values of K_w and K_b).

Ammonia can, therefore, conduct electricity only to a feeble extent. The dielectric constant of liquid ammonia (22) is much smaller than that of water (78.5). The lower dielectric constant results in a generally decreased ability of liquid ammonia to dissolve ionic compounds. Liquid ammonia is, therefore, a poor solvent for ionic substances. However, low viscosity of ammonia (0.254 centipoise at -33.5°C) compared to that of water (0.959 centipoise at 25°C) is expected to promote greater ionic mobilities and thereby compensate to some extent the effect of the comparatively low dielectric constant. The physical properties of water and liquid ammonia are given in Table.

Table: Physical Properties of Water and Ammonia.

Properties	**Water**	**Ammonia**
Boiling point	100°C	-33.5°C
Freezing point	0°C	-77.7°C
Density	1.0 g ml^{-1} (4°C)	0.68 g ml^{-1} (-33.5°C)
Dielectric constant	78.5 (25°C)	22.0 (-33.5°C)
Specific conductance (ohm^{-1} cm^{-1})	6.0×10^{-8} (25°C)	1×10^{-11} (-33.5°C)

Viscosity (centipoise)	0.959 (25°C)	0.254 (-33.5°C)
Dipole moment (Debye)	1.85	1.47
Trouton constant ($J\ K^{-1}\ mol^{-1}$)	109	101.2

Chemical Reactions in Liquid Ammonia

As mentioned above, liquid ammonia has water-like properties and hence the reactions which take place in aqueous solutions can also occur in liquid ammonia solutions. Chemical reactions that take place in liquid ammonia are of the following types.

1. **Precipitation reactions**. Precipitation reactions normally involve double decomposition. The solubilities of various substances in liquid ammonia and water are different and hence many reactions which are not normally possible in water have been reported to occur in liquid ammonia. Some of these reactions are discussed below.

a. Consider the precipitation of silver chloride in aqueous medium.

$$KCl + AgNO_3 \longrightarrow AgCl\downarrow + KNO_3$$

In liquid ammonia, the direction of the reaction is reversed.

$$AgCl + KNO_3 \xrightarrow{\text{liq. } NH_3} KCl\downarrow + AgNO_3$$

Similarly, a white precipitate of $BaCl_2$ is produced when solutions of silver chloride and barium nitrate in liquid ammonia are brought together.

$$AgCl + Ba(NO_3)_2 \xrightarrow{\text{liq. } NH_3} BaCl_2 \downarrow + 2AgNO_3$$

b. Iodides and bromides get precipitated when solutions of various metal nitrates and ammonium halides in liquid ammonia are mixed together.

$$Sr(NO_3)_2 + 2NH_4Br \xrightarrow{\text{liq. } NH_3} SrBr_2 \downarrow + 2NH_4NO_3$$

$$Zn(NO_3)_2 + 2NH_4I \xrightarrow{\text{liq. } NH_3} ZnI_2 \downarrow + 2NH_4NO_3$$

c. Ammonium sulphide in liquid ammonia is capable of precipitating many metal sulphides from the solutions of nitrates of the metals.

$$(NH_4)_2S + 2AgNO_3 \xrightarrow{\text{liq. } NH_3} Ag_2S \downarrow + 2NH_4NO_3$$

$$(NH_4)_2S + Cu(NO_3)_2 \xrightarrow{\text{liq. } NH_3} CuS \downarrow + 2NH_4NO_3$$

$$(NH_4)_2S + Cd(NO_3)_2 \xrightarrow{\text{liq. } NH_3} CdS \downarrow + 2NH_4NO_3$$

2. **Acid-Base Reactions in Liquid Ammonia**. There is an interesting comparison between neutralisation reactions in aqueous solution and in liquid ammonia solution. Hydrochloric acid gas dissolves in liquid ammonia giving NH_4^+ ions and Cl^- ions.

$$HCl\ (g) + NH_3 \longrightarrow NH_4^+ + Cl^-$$

A similar reaction takes place in the case of water.

$$HCl\ (g) + H_2O \longrightarrow H_3O^+ + Cl^-$$

In aqueous solution, the process of neutralisation of a strong acid by a strong base involves the combination of H_3O^+ and OH^- ions to form practically un-ionised H_2O, the anion of the acid and the cation of the base remaining unchanged. For instance, the neutralisation of hydrochloric acid with potassium hydroxide may be represented as

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$KOH \longrightarrow OH^- + K^+$$

$$H_3O^+ + OH^- \longrightarrow 2H_2O \text{ (Neutralisation)}$$

A similar thing happens in the case of liquid ammonia solution. The process of neutralisation involves combination of NH_4^+ and NH_2^- ions to form un-ionised NH_3. For instance, the neutralisation of ammonium chloride with potassium amide may be represented as

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

$$KNH_2 \longrightarrow K^+ + NH_2^-$$

$$NH_4^+ + NH_2^- \longrightarrow 2NH_3 \text{ (Neutralisation)}$$

Obviously, the role of NH_4Cl in liquid ammonia solution is the same as that of HCl in aqueous solution. Similarly, the role of KNH_2 in liquid ammonia solution is the same as that of KOH in aqueous solution. Thus, NH_4Cl may be regarded as a strong acid and KNH_2 as a strong base in liquid ammonia solution. They are termed as ammono acids and ammono bases, respectively.

3. **Amphoterism**. A compound that dissolves in acids and bases is said to be amphoteric in character. In aqueous medium, zinc and aluminium hydroxides are amphoteric. In liquid ammonia, zinc amide shows amphoteric behaviour. This is illustrated by the following reactions:

$$Zn(OH)_2 + 2HCl \xrightarrow{H_2O} ZnCl_2 + 2H_2O$$

$$Zn(NH_2)_2 + 2NH_4Cl \xrightarrow{\text{liq. } NH_3} ZnCl_2 + 4NH_3$$

$$Zn(OH)_2 + 2NaOH \xrightarrow{H_2O} Na_2ZnO_2 + 2H_2O$$

$$Zn(NH_2)_2 + 2NaNH_2 \xrightarrow{\text{liq. } NH_3} Na_2Zn(NH)_2 + 2NH_3$$

4. **Ammonolysis**. Ammonolysis in liquid ammonia is similar to hydrolysis in aqueous medium. Just as in hydrolysis, the concentration of H^+ or OH^- ions increases due to interaction of

cations or anions of a salt with H^+ or OH^- ions furnished by autoionisation of H_2O, in ammonolysis, the concentration of either NH_4^+ or NH_2^- ions increases due to interaction of cations or anions of a salt with NH_4^+ or NH_2^- ions furnished by autoionisation of NH_3. Consider the hydrolysis of $CuSO_4$.

$$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$$

$$2H_2O + 2H_2O \rightleftharpoons 2H_3O^+ + 2OH^-$$

$$Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2$$

$$CuSO_4 + 4H_2O \rightleftharpoons Cu(OH)_2 + SO_4^{2-} + 2H_3O^+$$

Weak base

$$SnCl_4 \longrightarrow Sn^{4+} + 4Cl^-$$

$$4NH_3 + 4NH_3 \rightleftharpoons 4NH_4^+ + 4NH_2^-$$

$$Sn^{4+} + 4NH_2^- \longrightarrow Sn(NH_2)_4$$

$$SnCl_4 + 8NH_3 \rightleftharpoons Sn(NH_2)_4 + 4NH_4^+ + 4Cl^-$$

Weak base

In ammonolysis, the atom or ion from the compound undergoing ammonolysis is replaced by $-NH_2$ or $=NH$ or $\equiv N$ group.

5. **Ammonation and formation of Ammoniates**. Ammonation is a type of solvation reaction in which liquid ammonia is used as a solvent and in which one or more ammonia molecules are attached to a solute species (a cation, an anion or a neutral molecule) by a chemical bond. The products of solvation are called solvates and in the case of

ammonation they are known as ammoniates. Salvation in water is called hydration and the products are known as hydrates.

Formation of typical ammoniates is shown below:

$$SO_3 + 2NH_3 \longrightarrow SO_3.2NH_3 \quad 1{:}2 \text{ adduct}$$

$$SiF_4 + 2NH_3 \longrightarrow SiF_4.2NH_3 \quad 1{:}2 \text{ adduct}$$

$$BF_3 + NH_3 \longrightarrow BF_3.NH_3 \quad 1{:}1 \text{ adduct}$$

6. **Complex Formation Reactions**. Several complex formation reactions in liquid ammonia are known. These are similar to reactions occurring in aqueous systems. The following reactions are given for illustration:

Aqueous System:

$$Zn(NO_3)_2 + 2NaOH \xrightarrow{H_2O} \underset{\text{Insoluble}}{Zn(OH)_2} + 2NaNO_3$$

$$Zn(OH)_2 + 2NaOH \xrightarrow{H_2O} \underset{\text{Soluble hydroxo complex}}{Na_2[Zn(OH)_4]}$$

Liquid Ammonia System:

$$Zn(NO_3)_2 + 2KNH_2 \xrightarrow{\text{liq. } NH_3} \underset{\text{Insoluble}}{Zn(NH_2)_2} + 2KNO_3$$

$$Zn(NH_2)_2 + 2KNH_2 \xrightarrow{\text{liq. } NH_3} K_2[Zn(NH_2)_4]$$

Soluble amide complex

Similarly, many metal amides, imides and nitrides dissolve in a solution of potassium amide in liquid ammonia forming soluble amide complexes.

$$AgNH_2 + KNH_2 \xrightarrow{\text{liq. } NH_3} K[Ag(NH_2)_2]$$

Soluble amide complex

Aluminium salts react with potassium amide solution in liquid ammonia forming soluble amide complexes. Thus,

$$AlCl_3 + 3KNH_2 \xrightarrow{\text{liq. } NH_3} Al(NH_2)_3 + 3KCl$$

Insoluble

$$Al(NH_2)_3 + KNH_2 \xrightarrow{\text{liq. } NH_3} K[Al(NH_2)_4]$$

Soluble amide complex

7. **Reduction Reactions**. Liquid ammonia serves as an excellent medium for reduction reactions involving inorganic species. For instance, alkali metals dissolve in liquid ammonia giving blue coloured solutions which are strong reducing agents as they can readily supply

electrons for reduction process. Sodium metal in liquid ammonia, for instance, reduces CuI to Cu.

$$CuI + Na \xrightarrow{\text{liq. } NH_3} Cu + NaI$$

8. **Oxidation Reactions**. Oxidising action of various oxidising agents is weaker in liquid ammonia than in aqueous solutions. For instance, HNO_3 in liquid ammonia does not act as an oxidising agent. Similarly, $KMnO_4$ in liquid ammonia acts as a very weak oxidising agent. $KMnO_4$ is reduced by a solution of potassium in liquid ammonia to K_2MnO_4 and finally to MnO.

$$K + NH_3 \longrightarrow KNH_2 + \tfrac{1}{2} H_2$$

$$6KMnO_4 + 6KNH_2 \longrightarrow 6K_2MnO_4 + 4NH_3 + N_2$$

$$K_2MnO_4 + 4K + 3NH_3 \longrightarrow MnO + 3KNH_2 + 3KOH$$

9. **Solubility of Substances in Liquid Ammonia**. As expected from its very low dielectric constant, liquid ammonia is a poor solvent for ionic substances. Amongst the inorganic compounds, nitrates, thiocyanates, perchlorates and most of the cyanides are soluble in liquid ammonia. Oxides, hydroxides, carbonates, phosphates, sulphates and most of the sulphides are insoluble. Most of the iodides are soluble and bromides are less soluble. Fluorides and chlorides (except Be^{2+} and Na^+ chlorides) are practically insoluble. Most of the ammonium salts such as NH_4NO_3, NH_4SCN, CH_3COONH_4 are soluble in liquid ammonia. Most of the metal amides, except those of alkali metals, are insoluble.Amongst the organic compounds, halogen compounds,

alcohols, ketones, esters, simple ethers, phenol and its derivatives are soluble. Aromatic hydrocarbons are sparingly soluble. Alkanes are insoluble. Alkenes and alkynes are slightly soluble. Amongst the elements, metals like Mg, Al, Zn, Ca, La, Ce, Mn, etc., have low solubilities in liquid ammonia. Alkali metals and alkaline earth metals are highly soluble in liquid ammonia. The non-metals like sulphur, phosphorus, iodine are soluble and they react with the solvent.

Solutions of Alkali metals in Liquid Ammonia. The ability to dissolve the alkali metals is one of the striking features of liquid ammonia as a solvent. The alkali metal solutions in liquid ammonia are blue in colour. The blue solution is characterised by

(i) Its colour which is independent of the metal involved.

(ii) Its density which is similar to that of pure liquid ammonia.

(iii) Its conductivity which is in the range of conductivities of electrolytes dissolved in liquid ammonia, and,

(iv) Its paramagnetism (i.e., these solutions when placed in a magnetic field are attracted into the field) which indicates the presence of a large number of unpaired electrons.

The alkali metal solutions dissociate to form alkali metal cations and ammoniated electrons. The dissociation into cation and ammoniated electron accounts for the electrolytic conductivity of the blue coloured dilute solutions. As the concentration of the solution is increased, M^+ and e^- species associate resulting in a decrease of conductivity.

Very dilute solutions of alkali metals in liquid ammonia are metastable and when catalysed they undergo decomposition.

$$[e(NH_3)_x]^- \xrightarrow{Fe_2O_3} NH_2^- + \tfrac{1}{2} H_2 + (x-1)\, NH_3$$

As the concentration of metal increases, the blue colour changes to bronze and finally the colour disappears altogether. On evaporating the alkali metal-ammoia solutions, the alkali metal can be recovered. The blue colour of dilute metal-ammonia solutions is attributed to the presence of ammoniated cation as well as ammoniated electron.

$$M^+ + xNH_3 \rightleftharpoons M(NH_3)_x^+$$

Ammoniated cation

$$e^- + yNH_3 \rightleftharpoons e(NH_3)_y^-$$

Ammoniated electron

Advantages of Liquid Ammonia as a Solvent

1. Dissolution of alkali metals in liquid ammonia without chemical reaction is the greatest advantage of using liquid ammonia as a solvent. The dissolved alkali metals can be recovered from the solution by evaporation.
2. The alkali metal solutions in liquid ammonia are strong reducing agents, even stronger than hydrogen.
3. Ammonium salts dissolved in liquid ammonia find application in preparative chemistry. They can be used to precipitate sulphides, halides, sulphates and alcoholates.
4. The tendency for solvolysis is less in liquid ammonia than in water.

Limitations of Liquid Ammonia as a Solvent

1. Low temperature or high pressure is necessary while working with liquid ammonia. This is because the liquid range for liquid ammonia is from -33.5^{o}C to -77.7^{o}C.
2. Liquid ammonia is hygroscopic in nature. Hence, all the reactions are to be carried out in sealed tubes.
3. The use of liquid ammonia as a solvent and as a reaction medium requires special technique as it has an offensive odour.