CHB-402 - By dr. Seema Pratap

Non-aq. solvents : Physical Properties of a solvent for functioning as an effective reaction medium, types of solvents and their general characteristics. Liq. NH_3 as a non-aq. solvents.

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Non - Aqueous Solvents — (1)

Solvent – A solvent is defined as a substance which has the power of dissolving other substances.* Water is an excellent solvent.

There are several physical properties of a solvent that are of importance in determining its behaviour. Two of the most important from a pragmatic point of view are the melting and boiling points. These determine the liquid range and hence the potential range of chemical operations. Most fundamental is the permittivity (dielectric constant). A high permittivity is necessary if solutions of ionic substances are to form readily. Coulombic attractions between ions are inversely proportional to the permittivity of the medium: $E = \frac{q^+ q^-}{4\pi r \varepsilon}$

* On account of its high dielectric const, it is capable of reducing forces of electrostatic attraction binding the charged ions in electrolytes in the solid state (ionization properties). Water has a long liq. range (0°C to 100°C) and hence is liq. at ord. temps. It is most easily available and can be easily purified. It is neutral, colourless, non-toxic and non-poisonous. Due to all these characteristics, water serves as the most useful solvents.

Attempts have been made to find out some other common substances which could serve as good solvents like water and could also have a sizeable dielectric const. so that they could have high ionising capacities. {* The various solvents are gen. classified as follows: →

Classification of Solvents* – (1) **Protonic and Aprotic solvents**

Solvents from which protons (i.e. H^+ ions) can be derived are called protonic solvents. Common examples are: H_2O, NH_3, HF, H_2SO_4 acid etc.

Aprotic solvents are: CCl_4, C_6H_6, acetonitrile, BF_3, liq SO_2 etc.

(2) Acid solvents, Basic solvents and Amphiprotic solvents; → Solvents having strong tendency to give protons are known as Acid solvents, e.g. liq. HF, H_2SO_4 and CH_3COOH etc. Solvents which have a strong affinity for protons are called basic solvents, e.g. liq. NH_3, pyridine, hydrazine etc. Amphiprotic Solvents are those which neither have a strong tendency to gain nor loose protons. Examples are: H_2O, CH_3OH, C_2H_5OH etc.

(3) Ionising and Non-ionizing solvents: → Ionising solvents are those which are capable of undergoing auto or self-ionization. Ex. are: $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$; $NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$;

$SO_2 + SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$ etc.

Solvents which do not ionise at all are non-ionizing solvents. They have low dielectric const. and are non-polar.

Characteristic Properties of a Solvent

— Some characteristic physical and chemical properties of a solvent which govern its usefulness as a solvent are as follows;

1 — Melting point and Boiling point — The melting and boiling points of a solvent indicate the range of temperature over which it can exist in the liq-state under atmosp. pressure.

Table 1

Solvent	M.P. (°C)	B.P. (°C)	Critical temp. (°C)	Critical press. (atm)
water	0	100.0	374.0	217.7
NH_3	−77.7	−33.5	132.4	112.0
SO_2	−75.5	−10.1	157.5	77.8
HF	−89.4	19.5	230.2	—
N_2O_4	−11.2	21.1	—	—

For each gas there is a certain temp. above which it cannot be liquefied, no matter how high a pressure may be applied. This temp. is known as the Critical temp. Thus, the C.T. of a gas may be defined as that temp. above which it cannot be liquefied howsoever high the pressure may be.

At the C.T. a certain pressure is needed to liquefy the gas. This pressure is called the C.P.. For ex., at 31.1°C (C.T.) CO_2 can be liquefied under a pressure of 72.9 atm. Thus the C.P. of the gas is 72.9 atm.

Because of the above values while water exists as liquid at ord. temp & pr., NH_3, SO_2 and N_2O_4 exist as gases under these condition. These gases, therefore, act as solvents only at low temps.

2) <u>Heats of fusion and vaporisation</u> — The heat absorbed by one mole of a substance to change from solid to liq. state is called its molar heat of fusion. Likewise, the heat absorbed by ~~so~~ one mole of a substance to change from liq. to vapour state is called its molar heat of vaporisation. The heats of fusion and vaporisation indicate the nature and strength of forces with which the molecules of the solvent are held together in the solid or the liq.-state. The high heat of vap. of a liq. indicates that the intermolecular binding forces in it are strong. A better idea of the intermolecular binding forces is obtained by dividing the heat (in joules) of vap. by the B.P. (K). For unassociated ~~normal~~ liquids this ratio is a constant known as <u>Trouton constant</u>. This const. is about ~ 90 $JK^{-1}mol^{-1}$ for unassociated ~~normal~~ liquids. Such liqs have single molecules without any bonds between them. A higher value of the const. indicates association of molecules. The molecules of liquids which undergo association are polar - (water - 109, NH_3 - 101.2), HF and alcohols are also associated liquids.

<u>Table 2</u>

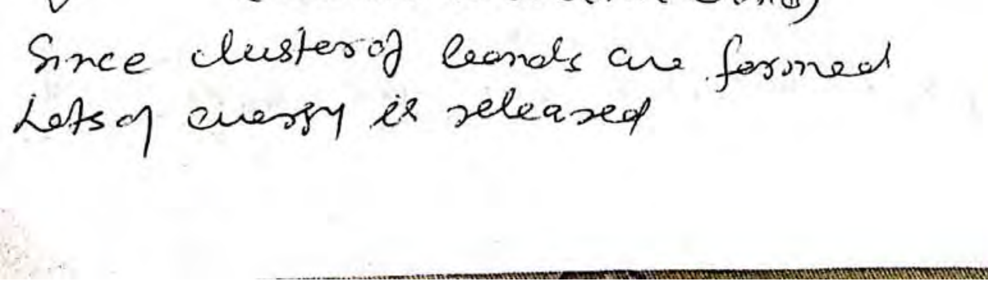
Solvents	Molar heat of Fusion (kJ/mole)	Molar heat of Vap at B.P. (kJ/mole)	Trout. Const.
water	6.02	40.65	109.0
NH_3	5.65	23.34	101.2
SO_2	7.40	24.93	
HF	4.58	30.28	

It is evident from <u>Table 2</u> that heats of fusion for water & NH_3 are very nearly the same. This indicates that the forces which hold molecules together in water and NH_3 are of the same magnitude. The heat of F. of SO_2 is comp. high while that of HF is comp. low indicating that while the force holding SO_2 molecules together is stronger, the force holding HF molecules is weaker,

3. **Dielectric Constant** – The coulombic force F between a cation and an anion is given by the expression $F = q_1 q_2 / [D(r_1 + r_2)^2]$ where q_1 and q_2 are the charges for cations and anions, respectively; r_1 and r_2 are the radii of the two ions and D is the dielectric const. A high value of D indicates that a small amount of energy will be required to seperate the ions and hence it will be easy to dissolve an ionic solute. Thus, dielectric const, in gen. determines the ability of a solvent to dissolve an ionic solutes. For ex, solvents such as anhydrous HF and water, which have high dielectric const, are the best solvents for ionic and polar compds. On the other hand solvents like liq. NH_3 and liq. SO_2 with low dielectric const. show decreased ability to dissolve ionic compds especially those containing multi-charged ions. Thus, carbonates, sulphates and phosphates are practically insoluble in liq. NH_3 and liq. SO_2.

The dielectric const. and the polarity of a solvent are closely related. An ionising solvent not only has a large dipole moment but also has a large dielectric const.

Solvent	Dipole Mom. (Debye units)	Dielec. const.
water	1.85	78.5 (25°C)
NH_3	1.47	22.0 (-33.5°C)
SO_2	1.61	17.4 (-20°C)
HF	1.9	83.6 (0°C)
N_2O_4	–	2.42 (0°C)



Since clusters of bonds are formed
Lots of energy is released

Liquid NH_3 — Liq. NH_3 is ~~the~~ one of the most extensively studied
Liq. Range (−33.5 – −77.5°C) non-aq. solvents ^[It is a protonic solvent] and its water like properties have made it a ~~slightly~~ highly useful solvent and a reaction medium for carrying out several types of org. and inorg. reactions. It shows a striking resemblance with water in its solvent action. NH_3 molecules are, however, less strongly associated through hydrogen-bonding in liq. NH_3. Consequently the freezing and boiling points of liq. NH_3 are lower than those of water. Another similarity with H_2O is the polarity of the NH_3 molecule. It has a pyramidal str. which makes it polar. A third similarity is autoionization of liq. NH_3, similar to the autoionization of water. Both liq. NH_3 and water show comparable autoionization, represented as under:

$$H_2O \rightleftharpoons H^+ + OH^-;\ H^+ + H_2O \rightleftharpoons H_3O^+ \Big\} \rightarrow 2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C$$ {Hydronium ion, hydroxyl ion.}

$$\left.\begin{array}{l} NH_3 \rightleftharpoons H^+ + NH_2^- \\ H^+ + NH_3 \rightleftharpoons NH_4^+ \end{array}\right\} \rightarrow 2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

Ammonium ion, Amide ion.

However, the extent of autoionization of liq. NH_3 is less than that of water

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

NH_3 can, therefore, conduct electricity only to a feeble extent. The dielectric const. of liq. NH_3 (22) is much smaller than that of water (78.5) which gen. results in low solubility of ionic compds in this solvent. However, low viscosity of NH_3 (0.254 cp at −33.5°C) compared to that of water (0.959 cp at 25°C) is expected to promote greater ionic mobilities and thereby compensate to some extent the effect of the dielectric const.

CHEMICAL Reactions In liq. NH_3 ⟶ Since NH_3 has water-like properties and hence the reactions which take place in aq. solutions can also occur in liq. NH_3 solutions.

1. pptation reaⁿs → pptation reactions normally involve double decompositions. The solubilities of various substances in liq. NH_3 and water are different and hence many reaⁿs which are not normally possible in water have been reported to occur in liq. NH_3. For ex.

(a) consider the pptation of AgCl in aq. medium.

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

In liq. NH_3, the direction of the reaction is reversed.

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

Similarly a white ppt of $BaCl_2$ is produced when solutions of silver chloride and barium Nitrate in liq. NH_3 are brought together.

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

(b) Iodides and bromides get ppted when solutions of various metal nitrates and ammonium halides in liq. NH_3 are mixed together.

$$Sr(NO_3)_2 + 2NH_4Br \xrightarrow{liq. NH_3} SrBr_2\downarrow + 2NH_4NO_3; \quad Zn(NO_3)_2 + 2NH_4I \xrightarrow{liq. NH_3} ZnI_2 + NH_4NO_3$$

(c) Amm-sulphide in liq. NH_3 is capable of pptation many metal sulphides from the solⁿs of their nitrates.

$$(NH_4)_2S + 2MNO_3 \longrightarrow Ag_2S \text{ or } MS + NH_4NO_3$$

$(M = Ag^+, Cu^{2+}, Cd^{2+})$

(2) Acid-Base reaⁿs in liq. NH_3 — There is an interesting comparison between neutralization reaⁿ in aq. solⁿ and in liq. NH_3 solⁿ. HCl gas dissolves in liq. NH_3 giving NH_4^+ and Cl^- ions.

$$HCl(g) + NH_3(liq) \longrightarrow NH_4^+ + Cl^- \quad \text{which is similar to } H_2O$$

$$HCl(g) + NH_3 \text{ " } \longrightarrow H_3O^+ + Cl^-$$

In aq. solⁿ, the process of neutralization of a strong acid by a strong base involves the combination of H_3O^+ and OH^- ions to form practically un-ionized water. The anion of the acid and the cation of the base remaining unchanged. For ex.

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

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

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