E-Content Study Material

B. Sc. Chemistry (H)

2nd Year

Paper II B

Inorganic Chemistry

Chapter VIII: Non-aqueous Solvents

Topic: Properties and Types of Solvents

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Solvent

A solvent is defined as a substance which has the power of dissolving other substances. Water is an excellent solvent. On account of its high dielectric constant, it is capable of reducing forces of electrostatic attraction binding the charged ions in electrolytes in the solid state. Thus, salts and other electrolytes get dissociated into ions when they dissolve in water and the solutions conduct electricity. Water has a long liquid range (0 to 100 ^{o}C) and hence is liquid at ordinary temperature. It is most easily available and can be easily purified. It is neutral, odourless, non-toxic and non-poisonous. It can, therefore, be handled safely. Due to all these characteristics, water serves as the most useful solvent.

Attempts have been made to find out some other common substances which could serve as good solvents like water and could also have sizeable dielectric constants so that they could have high ionizing capacities. Liquid ammonia, liquid sulphur dioxide, anhydrous hydrogen fluoride, anhydrous sulphuric acid and liquid dinitrogen tetroxide are some such solvents.

Types of Solvents

The various solvents are generally following types.

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, etc. Solvents from which protons cannot be ordinarily derived are called aprotic solvents. Examples are: CCl_4, C_6H_6, acetonitrile, etc.

2. **Acid solvents, basic solvents and amphiprotic solvents**. Solvents which have a strong tendency to give protons are also called acid solvents, e.g., liquid hydrogen fluoride, sulphuric acid and acetic acid. Solvents which have strong affinity for protons are called basic solvents, e.g., liquid ammonia, pyridine, hydrazine, etc. Amphiprotic solvents are those which neither have a strong tendency to gain nor a strong tendency to lose protons. Examples are: water, methyl alcohol, ethyl alcohol, etc.

3. **Ionising and non-ionising solvents**. Ionizing solvents are those which are capable of undergoing auto or self-ionisation.

Examples are: water, ammonia, sulphur dioxide, etc. These solvents ionize as follows:

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

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

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

Solvents which do not ionize at all are non-ionising solvents. Ionizing solvents have high dielectric constants and are polar. Non-ionising solvents have low dielectric constants 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 given below.

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 liquid state under atmospheric pressure. The melting and boiling points of various solvents alongwith their critical temperature and critical pressures are given in Table.

Table: Melting Points, Boiling Points and Critical Constants of Various Solvents.

Solvent	M.P./F.P. (^oC)	B.P. (^oC)	Critical temperature (^oC)	Critical pressure (atm)
Sulphuric acid	10.4	300.0	-	-
Water	0	100.0	374.0	217.7
Ammonia	-77.7	-33.5	132.4	112.0
Sulphur dioxide	-75.5	-10.1	157.5	77.8
Hydrogen fluoride	-89.4	19.5	230.2	-
Dinitrogen tetroxide	-11.2	21.1	-	-

Because of the above values while water exists as liquid at ordinary temperature and pressure, ammonia, sulphur dioxide and dinitrogen tetroxide exist as gases under these conditions. These gases, therefore, act as solvents only at low temperatures.

2. **Heats of fusion and vaporisation**. The heat absorbed by one mole of a substance to change from solid to liquid state is called its molar heat of fusion. Likewise, the heat absorbed by one mole of a substance to change from liquid to vapour state is called its molar heat of vaporisation. These constants for water, ammonia, sulphur dioxide and hydrogen fluoride are given in table.

Table: Molar Heats of Fusion and Vaporisation of some Solvents.

Solvents	Molar heat of fusion ($kJ\ mol^{-1}$)	Molar heat of vaporisation at boiling point ($kJ\ mol^{-1}$)
Water	6.02	40.65
Ammonia	5.65	23.34
Sulphur dioxide	7.40	24.93
Hydrogen fluoride	4.58	30.28

The heats of fusion and vaporisation indicates the nature and strength of forces with which the molecules of the solvent are held together in the solid or the liquid state. A high heat of vaporisation of a liquid indicates that the intermolecular forces in it are strong. A better idea of the intermolecular forces is obtained by dividing the heat of vaporisation by the boiling point. For normal liquids, the ratio of the heat of vaporisation expressed in joules to the boiling point (K) is a constant known as Trouton constant. This constant is about 90 $J\ K^{-1}\ mol^{-1}$ for normal liquids. Such liquids have single molecules without any bonds between them. A higher value of the constant indicates association of molecules. The molecules of liquids which undergo association are polar. The common solvents like water, ammonia, hydrogen fluoride and alcohols are all associated liquids.

It is evident from Table that heats of fusion for water and ammonia are very nearly the same. This indicates that the forces which hold molecules together in water and ammonia are of the same magnitude. The heat of fusion of sulphur dioxide is comparatively high while that of hydrogen fluoride is comparatively low indicating that while the forces 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

$$F = q_1q_2 / [\mathcal{E} (r_1 + r_2)^2]$$

Where q1 and q2 are the charges for cations and anions, respectively; r1 and r2 are the radii of the two ions and Ɛ is the dielectric constant. A high value of Ɛ indicates that a small amount of energy will be required to separate the ions and hence it will be easy to dissolve an ionic solute. Thus, dielectric constant, in general, determines the ability of a solvent to dissolve ionic compounds. For example, solvents such anhydrous hydrogen fluoride and water, which have high dielectric constants, are the best solvents for ionic and polar compounds. On the other hand, solvents like liquid ammonia and liquid sulphur dioxide with low dielectric constants show decreased ability to dissolve ionic compounds especially those containing multi-charged ions. Thus, carbonates, sulphates and phosphates are practically insoluble in liquid ammonia and liquid sulphur dioxide.The dielectric constant 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 constant. This is evident from the data given in Table.

Table: Dipole Moments and Dielectric Constants of Some Solvents.

Solvents	**Dipole Moment (Debye Units)**	**Dielectric Constant**
Water	1.85	78.5 (25 ^{o}C)
Ammonia	1.47	22.0 (-33.5 ^{o}C)
Sulphur dioxide	1.61	17.4 (-20 ^{o}C)

Hydrogen fluoride	1.90	83.6 (0 ^{o}C)
Dinitrogen tetroxide		2.42 (0 ^{o}C)