3. Determination of Solubility Class

Introduction

Solubility class determination gives an **idea** about

1. The type of the functional group present in the compound
2. The polarity and molecular weight of the compound
3. The nature of the compound (acidic, basic, neutral).

This is accomplished by testing the solubility of the compound in either of the following sets of solvents:

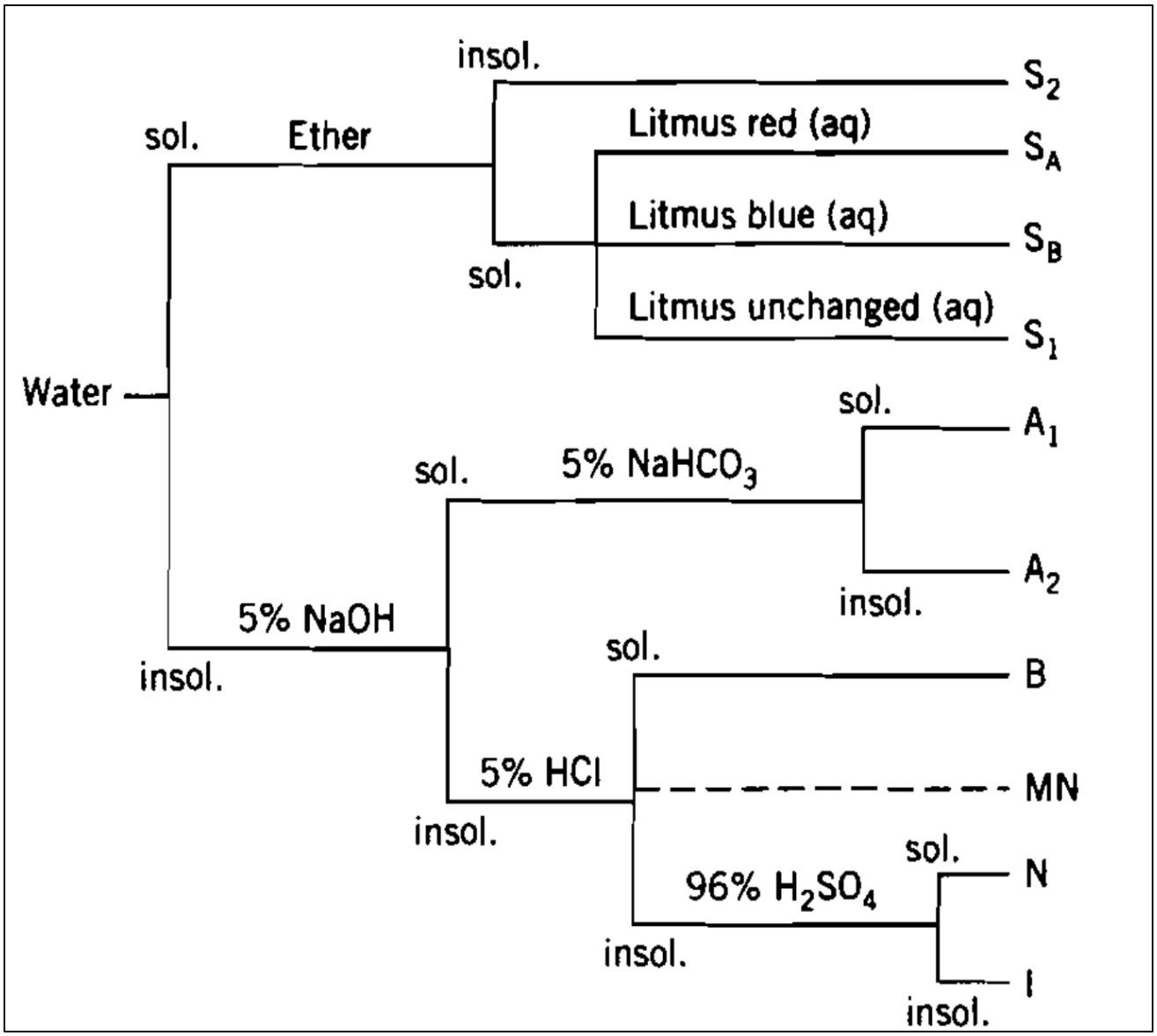
- Distilled water
- **5%** sodium hydroxide solution
- **5%** sodium bicarbonate solution
- **5%** hydrochloric acid solution
- Cold concentrated sulfuric acid
- Distilled water and ether

It is well known that hydrocarbons are insoluble in water because of their non-polar nature. If an unknown compound is partially soluble in water, then this indicates that a polar functional group is present. Additionally, solubility in certain solvents often leads to more specific information about the functional group. For example, benzoic acid is insoluble in water, but is converted by ***5% sodium hydroxide solution*** to a salt, sodium benzoate, which is readily water soluble. In this case, then, the solubility in ***5% sodium hydroxide solution*** of a water insoluble unknown is a strong indication of an acidic functional group. Prediction of the molecular weight and size may sometimes be obtained from the result of solubility tests. For example, in many homologous series of monofunctional compounds, the members with fewer than about five carbon atoms are water soluble, whereas the higher homologs are insoluble.

The first step to follow is to test the solubility of the compound in water. Generally and for solubility classification purposes, the compound is said to be soluble in any solvent if it dissolves to the extent of about **(0.1 gm/3ml) or (0.2 mL/3mL)**. This is achieved by dissolving

about **0.1gm** of the solid compound or **3-4 drops** of the liquid compound in gradually increasing volumes of the solvent up to **3ml (max. allowed volume is 3ml)** with shaking. This technique is the one that should be followed in solubility classification to determine whether the compound is soluble or insoluble in that solvent.

When solubility in dilute acid or dilute base is being considered, the significant observation to be made is whether it is significantly more soluble in aqueous acid or aqueous base than in water. Such increased solubility is the desired positive test for acidic or basic functional groups. Below is a very useful scheme for solubility classification:



Discussion on solvents

1. Water

Water is a polar solvent with a dielectric constant equals to 80. It has the ability to form hydrogen bonding and can act either as an acid or a base.

Therefore it can dissolve:

- Salts of ammonium ion **(RNH_3^+)** or organic acids salts with alkali metal cations **($RCOO^-$)**.
- Ionic compounds.
- Polar compounds "like dissolves like".
- Organic compounds with low molecular weight (**5** or less carbon atoms) such as alcohols, aldehydes, ketones, and carboxylic acids.

Water is useful to determine the degree of acidity of a compound, even if the compound is insoluble in water, using litmus paper (acidic, basic, or neutral).

Water is the first solvent used to determine the solubility class of a compound. If the compound is water soluble, the next step is to test its solubility in ether.

2. Ether

Ether is a non-polar solvent having a dielectric constant of 4.3. It cannot form hydrogen bonding (unassociated liquid). Therefore, it differs from water in that it cannot dissolve ionic compounds such as salts. It dissolves most water insoluble compounds; therefore, in the determination of solubility class, the importance of ether is for water-soluble compounds only and no further solubility tests using the remaining solvents are to be done.

Accordingly two probabilities are there:

a. Compounds soluble in both water and ether. These compounds:

- are monofunctional carboxylic acid with **5** or less carbon atoms and aryl sulfonic acids.. this class will called S_A and make blue litmus paper red.

- are monofunctional amines with **5** or less carbon atoms.. this class will called S_B and make red litmus paper blue.
- are monofunctional alcohols, aldehydes, ketones, esters, amides with **5** or less carbon.. this class will called S_1 and not change litmus paper.

b. Compounds soluble in water only (but not in ether). These compounds:

- are ionic [salts of organic acid, amine hydrochloride, amino acids]
- contain two or more polar groups with no more than four carbon atoms per each polar group such as carbohydrates, polyhydroxy compounds.

This group is classified as S_2 class.

Note that solubility in ether is tested only for water-soluble compounds.

3. 5% NaOH & 5% $NaHCO_3$

Water insoluble compounds must be tested first in 5% sodium hydroxide solution which is a basic solvent. It reacts with water insoluble compounds that are capable of donating protons such as strong and weak acids. The stronger the acid, the weaker the base it can react with. Water insoluble compounds that dissolve in **5%** sodium hydroxide solution must also be tested for solubility in **5%** sodium bicarbonate solution. Therefore, for water insoluble acidic compounds sodium hydroxide solution is considered as a ***detecting solvent*** whereas sodium bicarbonate solution is called as a ***sub classifying solvent*** since it can react with strong acids only.

That is, these two solvents give an idea about the acidity degree of the compound. Note that testing solubility in **5%** sodium bicarbonate solution is not needed if the compound is insoluble in **5%** sodium hydroxide solution, but rather, **5%** hydrochloric acid solution should be used.

Two probabilities are there:

a. Compounds soluble in both bases. This group is given class A_1. This class includes strong acids that have the ability to react with weak bases which carboxylic acids with

more than **5** carbon atoms, nitrophenols, aldehydophenols and polyhalophenols in which protons are weakly attached and can be given easily.

b. Compounds soluble in **5%** sodium hydroxide solution only. This group is given class ***A_2*** [weak organic acids] and it includes phenols, imides, thiophenols, sulfonamides; all with more than **5** carbons.

4. 5% HCI

If the compound is insoluble in water and sodium hydroxide solution (and, hence, insoluble in sodium bicarbonate solution too), this means that the compound is not an acid but, rather, is either a basic compound or a neutral compound. **5%** hydrochloric acid solution, which can dissolve basic compounds such as amines **(RNH_2)**, is used for such a compound. If the compound is soluble in this solvent, then it is given class ***B***. This class includes [primary, secondary, tertiary] amines and anilines.

5. Cold concentrated H_2SO_4

If the compound is insoluble in water, **5%** sodium hydroxide solution, and **5%** hydrochloric acid solution, solubility in cold concentrated sulfuric acid should be tested. If the compound is soluble in this acid, it belongs to class ***N*** which includes monofunctional neutral compounds (containing oxygen with more than **5** carbon atoms) such as alcohols, aldehydes, ketones, esters, and ethers, unsaturated hydrocarbons [alkynes and alkenes], or some aromatic hydrocarbons especially those with activating group. On the other hand, compounds that are insoluble in cold concentrated sulfuric acid belong to class ***I*** which includes inert aliphatic saturated hydrocarbons, aromatic hydrocarbons, haloalkanes, aryl halides and diaryl ether.

HOMEWORK

1. Show by a chemical equation only how can concentrated sulfuric acid dissolve oxygen containing neutral compounds.
2. Depending on the chemical structure discuss your results of solubility class of the compounds given to you.