SOLUBILITY OF ORGANIC COMPOUNDS

OTHER DOCUMENTS:

Experimental procedure, Extraction (technique), Report template, Report QU

INTRODUCTION

The objective of this experiment is to investigate the solubility of some simple "unknown" organic molecules containing a variety of common organic functional groups. You will then explore the solubility implications in an important laboratory technique, extraction. Using the important relationship between the solubility properties of an organic molecule and its' structure, you will then be able to use the solubility results to assign each of the unknown organic compounds to a solubility class.

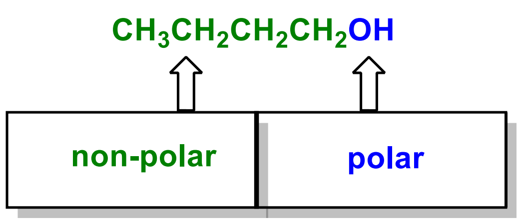
This experiment is based on the very important idea that **structure dictates function**. This means that the way the atoms in a molecule are connected together determines the properties of the molecule such as its solubility, acidity or basicity, stability, reactivity towards a particular species such as H+ *etc*. Interpreting (or predicting) the solubility of an organic molecule is a very useful skill. For example, most reactions are carried out in solution where a solvent needs to be used to dissolve the reactants to allow the molecules to be in the same phase so that the molecules can actually collide with each other and then react. The solvent also helps absorb and dissipate the heat released during the reaction. Solubility can be useful when trying to purify samples (*e.g.* recrystallisation: picking a suitable recrystallisation solvent) or isolate products from a multi-component reaction mixture (*e.g.* via **extraction**), or when extracting a molecule from a natural source such as a plant, or designing a new pharmaceutical that needs to be soluble in the blood stream (aqueous and alkaline), the stomach (aqueous and acidic) or enter the central nervous system ("fatty"). You will be using some of these topics and experimental techniques later this semester. For example, you will extract and then isolate caffeine from tea leaves - an "experiment" that you may perform several times per day while making tea or, similarly, for coffee from ground coffee! Solubility is also an important consideration when performing reactions to synthesise molecules; usually, reagents and starting materials are mixed together in a solution. The partitioning of drug molecules within the body between the blood and various tissues is also related to solubility properties.

Key practical things about solubility:

- Remember that the important phrase "**like dissolves like**" is referring to the **polarity** of the materials involved.(polarity controls solubility)
- Solubility of solids in liquids tends to increase with increasing temperature
- Mixing solvents can help modify polarity (*e.g.* adding water to ethanol makes the ethanol more polar)

Solubility at the molecular level

At the molecular level, solubility is controlled by the energy balance of intermolecular forces between solute-solute, solvent-solvent and solute-solvent molecules. Recall from general chemistry, that intermolecular forces come in different strengths ranging from very weak induced dipole – induced dipole interactions to much stronger dipole-dipole forces (including the important special case, hydrogen bonding). However there is a simple, very useful and practical empirical rule that is actually quite reliable. That simple rule is "**like dissolves like**" which is based on the **polarity** of the systems *i.e.* polar molecules tend to dissolve in polar solvents (*e.g.* water, alcohols) and non-polar molecules in non-polar solvents (*e.g.* the hydrocarbon hexane). This is why ionic compounds, like table salt (sodium chloride), or compounds like sugar, dissolve in water but do not dissolve to any great extent in most organic solvents. It also applies to the separation of oil and water (*i.e.* they are immiscible, *e.g.* think of a salad dressing). The polarity of organic molecules is determined by the presence of polar bonds[1] due to the presence of electronegative atoms (*e.g.* N, O) in polar functional groups such as amines (-NH_2) and alcohols (-OH). Overall, polarity is a balance of the non-polar parts and polar parts of a molecule, and it can be convenient to mentally break a molecule into its polar and non-polar regions. A larger, non-polar "organic" hydrocarbon part will tend to make the molecule less soluble in polar solvents while more polar parts will tend to make it more water soluble (polar solvent) and vice versa for non-polar solvents.



For example, consider the following solubilities of the straight chain alcohol series in water (g / L)[1]:

Methanol and ethanol : infinitely soluble	1-heptanol 1.6
1-propanol 1000	1-octanol 0.3
1-butanol 73	1-nonanol 0.13
1-pentanol 22	1-decanol 0.037
1-hexanol 5.9	1-dodecanol 0.004

The polar hydroxyl group (-OH) can interact favourably with structurally similar water molecules (via hydrogen bonding). Therefore, short chain alcohols are water soluble. But as the organic part gets larger (*i.e.* has more C atoms = a longer chain in this linear series), then this interaction is less effective and so the water solubility *decreases*. This trend is quite general and applies to other organic functional groups too.

Solubility Classification

Since the polarity of an organic molecule is related to the presence of polar bonds that are found within organic functional groups, the solubility characteristics of an organic compound can provide experimental evidence for the presence (or absence) of several important organic functional groups[*], as indicated in the chart below.

***Review the structure of common organic functional groups as part of your preparation for the laboratory session - note that functional groups[2] are covered by CAL351.1**

Most organic molecules are typically relatively non-polar and are usually soluble in less polar solvents. Organic solvents come in a range of polarities depending on the functional groups that they have present within their molecular structures. For example, methanol, CH_3OH is quite polar (note the structural similarity to water) and ethanol, CH_3CH_2OH, a little bit less so. Acetone (also known as propan-2-one, sometimes found in nail polish remover), $(CH_3)_2C{=}O$ is a moderately polar organic solvent while petroleum ether (a mixtures of alkanes) and hexanes are non-polar.

Solvent	Some solubility or complete miscibility
Water	alcohols, amines, acids, esters, ketones, aldehydes, etc. (typically only those with 5 carbons or fewer (*i.e.* low MW))
5% $NaHCO_3$	carboxylic acids
5% NaOH	carboxylic acids and phenols
5% HCl	amines
diethyl ether	most organic molecules

Thus, most organic molecules, which are typically relatively non-polar are usually soluble in organic solvents (*e.g.* ethyl acetate, diethyl ether, dichloromethane, chloroform, petroleum ether, hexanes *etc.*) but less soluble or insoluble in polar solvents like water and short chain alcohols. However, some organic molecules are more polar and therefore, more soluble in water. This denotes a rather high ratio of polar group(s) to the non-polar hydrocarbon chain, *i.e.*, a low molecular weight compound containing an -OH, -NH_2 or -CO_2H group, or a larger molecule containing multiple polar groups (*e.g.* a molecule of sucrose (sugar) $C_{12}H_{22}O_{11}$ with 8 hydroxyl groups (-OH) where at 20 ^{o}C, over 200g can be dissolved in just 100 mL of water!).

The presence of an acidic -CO_2H or a basic -NH_2 functional groups[3] in a water-soluble compound can be detected by measuring the pH of the solution (low (acidic) or high pH (basic) respectively or using an indicator paper such as litmus paper (preferred) or pH paper).

Compounds that contain acidic functional groups that are insoluble in water can become soluble in an aqueous environment if they form an ionic species when treated with a base. This is because the deprotonated ionic form is much more polar than the neutral form. Similarly, compounds that contain basic functional groups that are insoluble in water, can become soluble in an aqueous environment if they form an ionic species when treated with an acid. This is because the protonated ionic form is much more polar than the neutral form.

The solubility of carboxylic acids (typical pKa = 3 to 5) and phenols (pKa = 9 to 10) in aqueous sodium hydroxide (a base) is due to the formation of the polar (ionic) carboxylate or phenoxide groups respectively. Since acids and phenols are much stronger acids than water (pKa about 15), and therefore the acid-base equilibria lie far to the right (products), which is the **more polar** side for the organic species:

$$RCO_2H + OH^- \rightleftharpoons RCO_2^- + H_2O$$

$$ArOH + OH^- \rightleftharpoons ArO^- + H_2O$$

Carboxylic acids, but not phenols, are also stronger than carbonic acid, H_2CO_3, (pKa = 7), and therefore, carboxylic acids are also soluble in aqueous $NaHCO_3$ solution because they are also deprotonated by bicarbonate:

$$RCO_2H + HCO_3^- \rightleftharpoons RCO_2^- + H_2O + CO_2$$

The solubility of amines in dilute aqueous acid similarly reflects the fact that they are stronger bases than water, and are converted by protonation (*i.e*. reaction with a proton) to the more polar ammonium ion:

$$RNH_2 + H_3O^+ \rightleftharpoons RNH_3^+ + H_2O$$

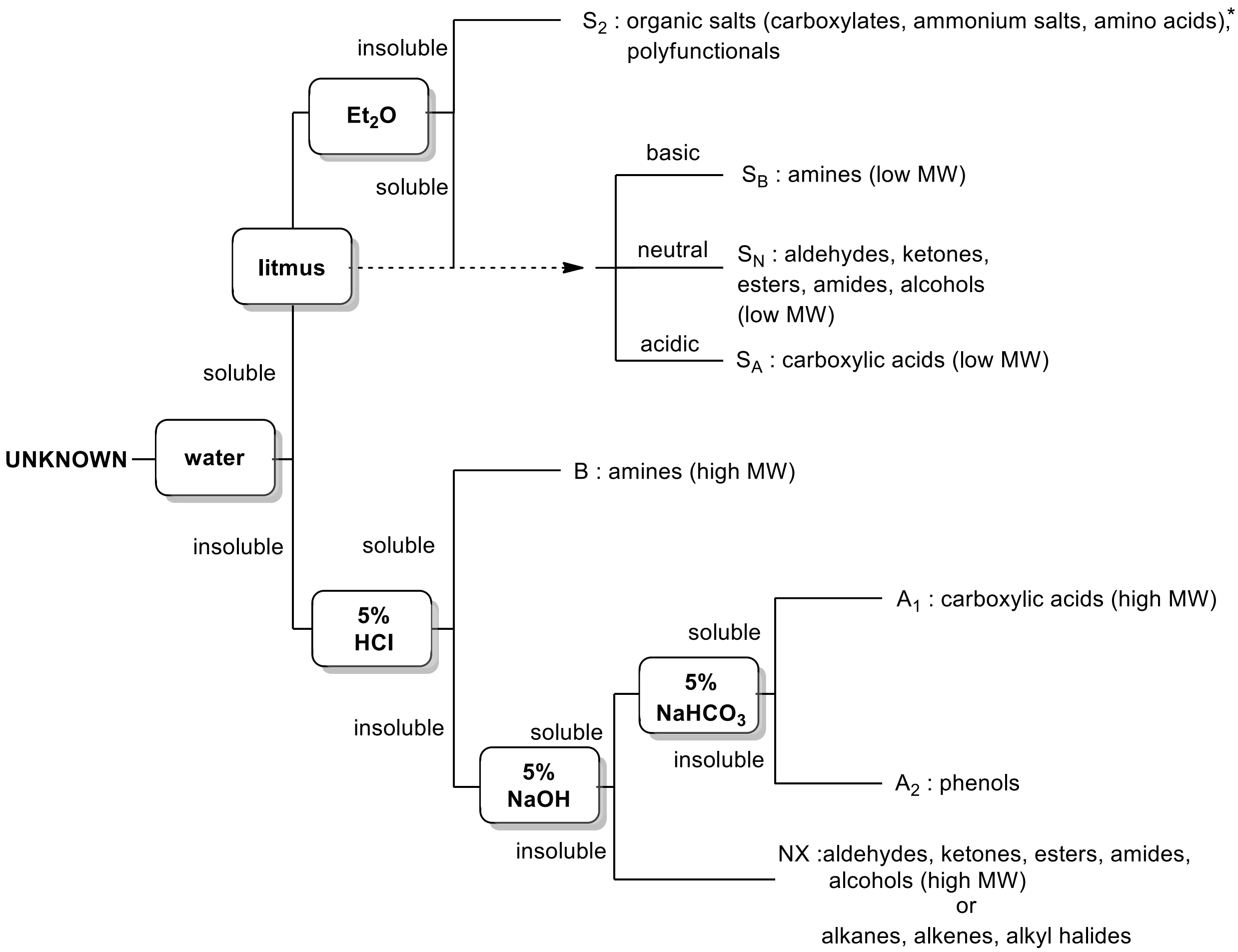
Amines are the only common class of organic compounds which are readily protonated in dilute aqueous acid.

These principles mean that the solubility behaviour of a compound in various solvents can be used to place it in a solubility class as represented in the figure below. As an example, a compound that is insoluble in water but soluble in 5%HCl is class **B**, a higher molecular weight amine.

In the Laboratory

During this experiment you will test the solubility of a series of unknown organic compounds (A-G). The unknowns are (in alphabetical order: benzamide, benzoic acid, glycine, naphthalene, sodium benzoate, thymol and p-toluidine). The solubility is tested in a series of solvent systems based on the pathways in the flow chart figure shown below. Each test will allow you to classify the organic compound as either **soluble** or **insoluble** in each of the test solvents, dictating which test to perform next and finally assign the unknown to a specific solubility class.

During the laboratory session, your TA will also introduce and discuss extraction relating it to solubility due to the partitioning of the materials into different immiscible solvents.



* Use litmus test results and / or additional 5%HCl or 5%NaOH tests to help provide further information

Flow diagram for solubility tests.

For example, a compound that is soluble in water, with a basic litmus test and soluble in ether would be in class S_B (low molecular weight amines).

REFERENCES

1. Values collected from Wikipedia for each alcohol *e.g.* Wikipedia : Methanol
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2. Functional groups
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