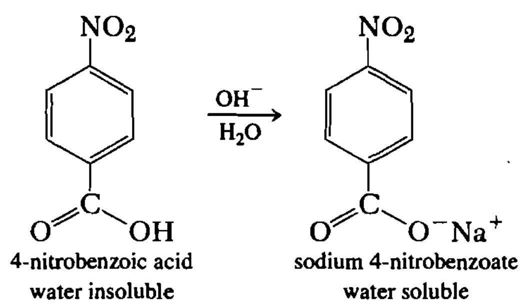
Classification of organic compounds By solubility

In this experiment we begin the process of determining the structural composition of organic compounds based upon interpretation of simple solubility tests can be extremely useful in organic structure determination. Before proceeding, the difference between solubility and a chemical reaction must be explain . In some cases, a chemical reaction is occur by a change in color or heat or by the formation of a precipitate. Solubility involves the formation of one layer, if the compounds are miscible, or two layers, if the compounds are immiscible.

The solubility of organic compounds can be divided into two major categories: solubility in which a chemical reaction is the driving force, for example, the following acid-base reaction,



and solubility in which simple miscibility is the only mechanism involved, such as dissolving ethyl ether in carbon tetrachloride. Although the two solubility sections below are interrelated, the first section deals primarily with the identification of functional groups and the second with the determination of solvents to be used in recrystallizations, spectral analyses, and chemical reactions.

SOLUBILITY IN WATER, AQUEOUS ACIDS AND BASES, AND ETHER

Three kinds of information can often be obtained about an unknown substance by a study of its solubility in water, 5% sodium hydroxide solution, 5% sodium bicarbonate solution, 5% hydrochloric acid solution, and cold concentrated sulfuric acid. **First**, the presence of a functional group is often indicated. For instance, because hydrocarbons are insoluble in water, the mere fact that an unknown is partially soluble in water indicates that a polar functional group is present. **Second,** solubility in certain solvents often leads to more specific information about the functional group. For example, benzoic acid is insoluble in a polar solvent, 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.

Finally, certain deductions about molecular size and composition may sometimes be made. 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.

Compounds are first tested for solubility in water. In considering solubility in water, a substance is arbitrarily said to be "soluble" if it dissolves to the extent of 3.3 g/100 mL of solvent.

If the compound is soluble in water, then it is tested for solubility in ether. If the compound is insoluble in ether, then it is in solubility class S_2. Solubility in ether indicates that the compound is in solubility classes S_A, S_B, or S_1 The aqueous solutions of the ether soluble compounds are then tested with pH paper to narrow down the choices. No more solubility tests are needed at this point if the compound is soluble in water.

However, if the compound is not soluble in water, then it is tested for solubility in 5% sodium hydroxide solution. Acidic compounds are identified by their solubility in 5% sodium hydroxide solution. Strong and weak acids (solubility classes A_1 and A_2; see Table.(1) and Figure (1) are differentiated by their solubility or lack of solubility in 5% sodium bicarbonate solution. Once the compound is identified as an acid and its solubility class determined, then no more solubility tests are needed.

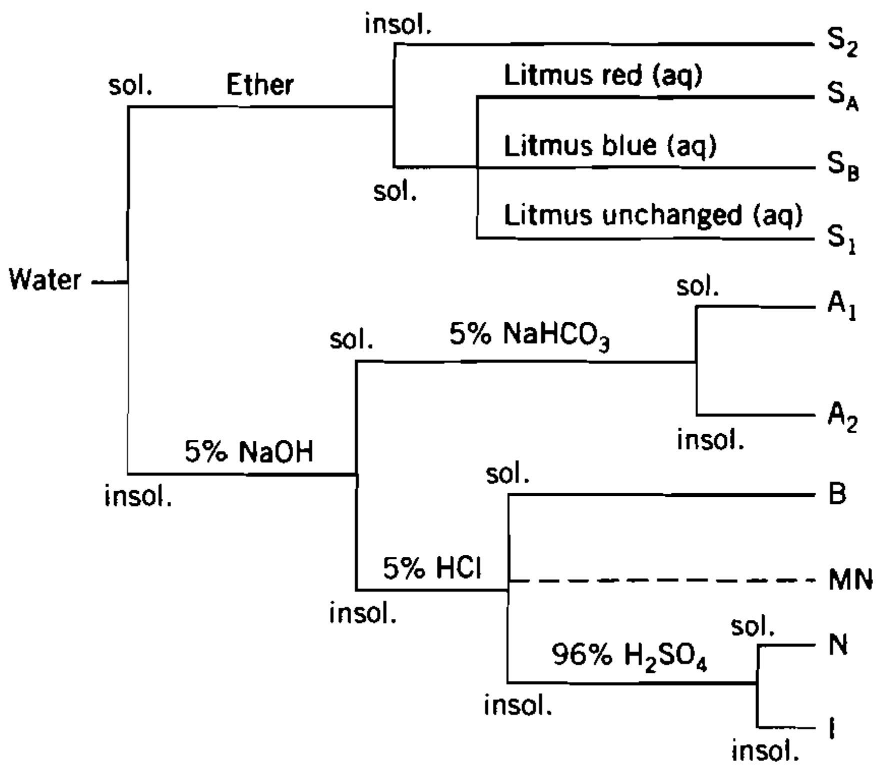


Figure (1) Classification of organic compounds by solubility: determination in water, acids, bases, and ethers (see Table 5.1 for compounds comprising each class), sol. = soluble, insol. = insoluble; litmus is red at pH below 4.5 and blue above 8.3.

TABLE .1 Organic Compounds Comprising the Solubility Classes

S_2	Salts of organic acids (RCO_2Na, RSO_3Na); amine hydrochlorides (RNH_3Cl); amino acids ; polyfunctional compounds with hydrophilic functional groups: carbohydrates (sugars), polyhydroxy compounds, polybasic acids, etc.
S_A	Monofunctional carboxylic acids with five carbons or fewer;
S_B	Monofunctional amines with six carbons or fewer.
S1	Monofunctional alcohols, aldehydes, ketones, esters, nitriles, or fewer.
A1	Strong organic acids: carboxylic acids with more than six withdrawing groups in the ortho and / or para position(s);
A2	Weak organic acids: phenols, enols, oximes, imides, more than five carbons; /3-diketones (1,3-diketones); nitro
B	Aliphatic amines with eight or more carbons; anilines (only one nitrogen); some ethers.
MN	Miscellaneous neutral compounds containing nitrogen or carbon atoms.
N	Alcohols, aldehydes, ketones, esters with one functional group fewer than nine carbons, ethers, epoxides, alkenes, alkynes, (especially those with activating groups).
I	Saturated hydrocarbons, haloalkanes, aryl halides, other diaryl ethers.
"Acyl	halides and carboxylic acid anhydrides have not been classified because of their high reactivity.

For compounds that are insoluble in water and subsequently insoluble in 5% sodium hydroxide, the solubility in 5% hydrochloric acid solution is determined. Compounds that behave as bases in aqueous solution are detected by their solubility in 5% hydrochloric acid solution (solubility class B). If the compound is identified as a base, then additional solubility tests are not needed.

Many compounds that are neutral toward 5% hydrochloric acid solution behave as bases in more acidic solvents such as concentrated sulfuric acid. In general, compounds containing sulfur or nitrogen have an atom with an unshared pair of electrons and would be expected to dissolve in a strong acid. Compounds that contain nitrogen or sulfur and are neutral in aqueous acid or base are placed in solubility class MN.

Compounds that are insoluble in water, 5% sodium hydroxide solution, and 5% hydrochloric acid solution, but soluble in 96% sulfuric acid solutions, are classified in solubility class N. The solubility in 96% sulfuric acid indicates the presence of an oxygen atom or of a reactive hydrocarbon function such as a double or triple bond or an easily sulfonated aromatic ring.

Compounds that are insoluble in water, 5% sodium hydroxide solution, 5% hydrochloric acid solution, and 96% sulfuric acid solution are placed in solubility class I (inert compounds).

When solubility in 5% acid or base is being considered, the significant observation to be made is not whether the unknown is soluble to the extent of 3% or to any arbitrary extent but, rather, whether it is significantly more soluble in aqueous acid or base than in water. This increased solubility is a positive test for a basic or acidic functional group.

Determination of Solubilities

Procedure for Water Solubility

1. Place 0.05 mL (approximately one drop) or 25 mg of the compound in a small test tube, and add 0.75 mL of water in small portions. Shake vigorously after the addition of each portion of solvent, being careful to keep the mixture at room temperature. If the compound dissolves completely, record it as soluble.
2. Powder all solids to increase the rate of dissolving of the solid. If the solid appears to be insoluble in water or ether, it is sometimes advisable to heat the mixture gently. If the solid dissolves with heating, the solution is cooled to room temperature and is shaken to prevent supersaturation.
3. Measure all liquids with a graduated pipet that permits the accurate measurement of the liquid.

Procedure for Testing with Litmus Paper

Dissolve 0.05 mL (approximately one drop) or 25 mg of the compound in 0.75 mL of water. Using a stirring rod, place a drop of this aqueous solution on both red and blue litmus paper. If both litmus papers turn red, the compound has a solubility class of S_A. If both litmus papers turn blue, the compound has a solubility class of S_B- If both litmus papers remain their original color, the compound has a solubility class of S_1.

Compounds with a pKa < 8 will fall in class S_A (see Table.1 and Figure(1). Compounds with a pKb < 9 will fall in class S_B- Consequently, phenols with pKa of about 10 give aqueous solutions too weakly acidic (pH about 5) to turn litmus paper red. Litmus is red at pHs below 4.5 and blue above

8.3. For similar reasons, an aromatic amine such as aniline is too weak a base (pKb 9.4) to turn litmus blue in aqueous solution. Although more refined procedures can be developed using a pH-indicating paper, it is preferable to rely more on the tests discussed in Chapter 9.

Cleaning Up : Place the test solutions in the aqueous solution container .

Procedure for Ether Solubility

Place 0.05 mL (approximately one drop) or 25 mg of the compound in a small test tube, and add 0.75 mL of diethyl ether in small portions. Shake vigorously after the addition of each portion of solvent, being careful to keep the mixture at room temperature. If the compound dissolves completely, record it as soluble.

Procedure for Solubility in Aqueous Acid or Base

To test for solubility in aqueous acid or base, thoroughly shake a mixture of 0.05 mL (approximately one drop) or 25 mg of the unknown compound with 0.75 mL of 5% sodium hydroxide solution, 5% sodium bicarbonate solution, or 5% hydrochloric acid solution. Separate (filter if necessary) the aqueous solution from any undissolved unknown, and neutralize it with acid and base. Examine the solution very carefully for any sign of separation of the original unknown. Even a cloudy appearance of the neutralized filtrate is a positive test.

Procedure for Solubility in Concentrated Acid:

Place 0.6 mL of concentrated sulfuric acid in a test tube, and add 0.05 mL (approximately one drop) or 25 mg of the unknown compound. For purposes of solubility classification, unknowns that react with sulfuric acid to produce heat and/or color changes should be classified as soluble, even if the sample does not appear to dissolve.

Cleaning Up Carefully neutralize the test solution with 10% sodium hydroxide solution and place the test solution in the aqueous solution container.

Theory of Solubility

Polarity and Solubility

When a solute dissolves, its molecules or ions become distributed more or less randomly among those of the solvent. In crystalline sodium chloride, for example, the average distance between sodium and chloride ions is 2.8 A. In a 1 M solution the solvent has interspersed itself in such a way that sodium and chloride ions are about 10 A apart. The difficulty of separating such ions is indicated by the high melting point (800°C) and boiling point (1413°C) of pure sodium chloride. Another indication of the importance of solvent is the fact that sodium chloride readily forms ions in water, while it takes several hundred kilocalories per mole to form ions from sodium chloride in the solid state.

The dielectric constant is the measure of the ability of the solvent to separate ionic charges. The dielectric constant of the solvent is related to the polarity of the solvent. Dielectric constants of some organic solvents are listed in Table 2. A compound with a high dielectric constant is a polar solvent; a compound with a low dielectric solvent is a nonpolar solvent. It is not surprising that water, with a high dielectric constant of 80, facilitates the separation of sodium and chloride ions and dissolves sodium chloride readily, whereas both hexane (dielectric constant 1.9) and diethyl ether (dielectric constant 4.4) are extremely poor solvents for ionic salts. However, this is not entirely the case. A high dielectric constant is required but is not the only characteristic of an effective ion solvent. For example, hydrogen cyanide, with a dielectric constant of 116, is a very poor solvent for salts such as sodium chloride. Although the situation is quite complex, one major factor responsible for the efficiency of water and other hydroxylic solvents is their ability to form hydrogen bonds with the solute.

TABLE .2 Dielectric Constants of Common Organic

Compound	Dielectric Constants
Hydrogen cyanide	116
Formamide	111
Water	80
Formic acid	58
Dimethyl sulfoxide	47.8
Acetonitrile	37.5
N,N-Dimethylforma	37
Methanol	32.6
Hexamethylphospho	30
Ethanol	24.3
Acetone	20.7
Methylene chloride	9
Tetrahydrofuran	7.6
Acetic acid	6.2
Ethyl acetate	6
Chloroform	4.8
Diethyl ether	4.4
Benzene	2.3
Carbon tetrachloride	2.2
Hexane	1.9

The high dielectric constant and hydrogen-bonding ability of water, which combine to make it a good solvent for salts, also make it a poor solvent for nonpolar substances. As a general rule, a polar solvent may be expected to readily dissolve only polar solutes, and nonpolar solvent only nonpolar solutes. This generalization has been summarized more succinctly as "like dissolves like."