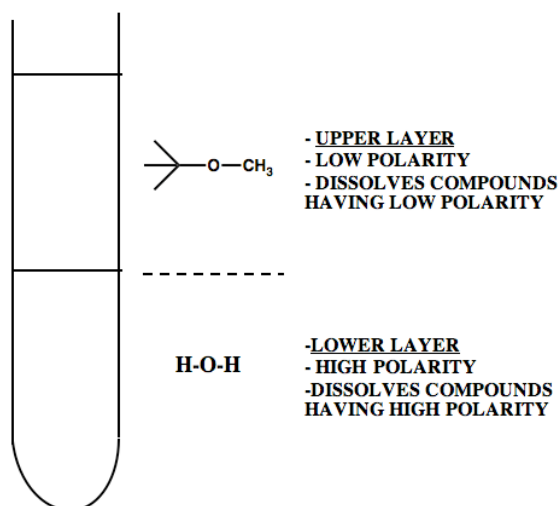


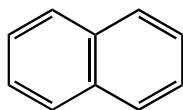
Acid-Base Extraction.

Extraction involves dissolving a compound or compounds either (1) from a solid into a solvent or (2) from a solution into another solvent. A familiar example of the first case is making a cup of tea or coffee - the soluble flavor and odor chemicals and caffeine are extracted from the solid tea leaves or ground coffee beans into hot water (the solvent). Insoluble plant material is left behind in the tea bag or coffee filter. An example of the second case is an experiment that is often done in an introductory organic lab - an organic solvent is used to extract the caffeine from an aqueous tea or coffee solution, leaving the more water-soluble compounds behind in the aqueous solution. This in fact is how decaffeinated tea and coffee are sometimes made.

An acid-base extraction, this week's experiment, is a modification of the second case above; that is, it is a solvent-solvent extraction. Before looking at what makes it an acid-base extraction, first consider solvent-solvent extractions in general. A requirement of a solvent-solvent extraction is that the two solvents be mostly insoluble in one another. That is, a mixture of the two solvents will separate into two layers. It is important to note that the upper layer is that which is less dense. For example, a mixture of *tert*-butyl methyl ether and water will separate into two layers, with the ether layer (density = 0.74) being on top of the water layer (density = 1.0). Note that in almost every case, one of the solvents is water or an aqueous solution. The other solvent is an organic solvent that is mostly insoluble in water. Examples include *tert*-butyl methyl ether, hexane, and dichloromethane. The organic solvent must also be volatile (easily-evaporated) so it can be easily removed by evaporation at the end.

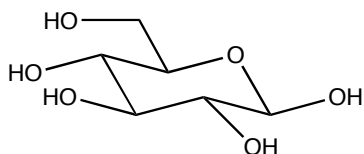


As an example of a separation that could be accomplished by using a solvent-solvent extraction, consider a mixture of two solid compounds, naphthalene and glucose.



Naphthalene

- low polarity
- high ether solubility
- low water solubility

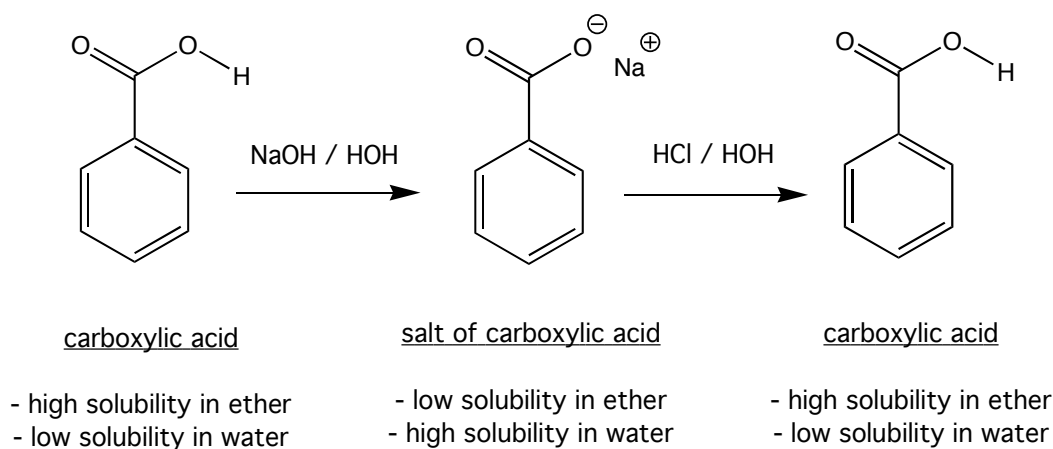


β -D-Glucopyranose

- high polarity/H-bonding
- low ether solubility
- high water solubility

If the mixture of naphthalene and glucose is dissolved in *tert*-butyl methyl ether and mixed well with water, the glucose will mostly dissolve in the lower water phase (phase = layer) and the naphthalene will mostly dissolve in the upper ether phase. The two phases can then be physically separated using a pipet and placed into two separate tubes. The water and ether can then be evaporated to yield the separated solid compounds. This is the gist of an extraction.

An acid-base extraction operates on the same principle, but can provide a further level of fine tuning. If one or more of the compounds in the mixture to be separated is acidic or basic, the solubilities of these acidic and basic components can be manipulated to our advantage by applying simple acid-base reactions. Using such a manipulation, an acidic or basic compound that may be ether soluble and water insoluble can be changed to be ether insoluble and water soluble by carrying out an acid-base reaction. The solubilities of acidic and basic compounds can thus be changed at will. Once the layers are separated as before, the neutral acid or base can be regenerated by yet another acid-base reaction. An example of such a manipulation of solubilities is shown below for a carboxylic acid.



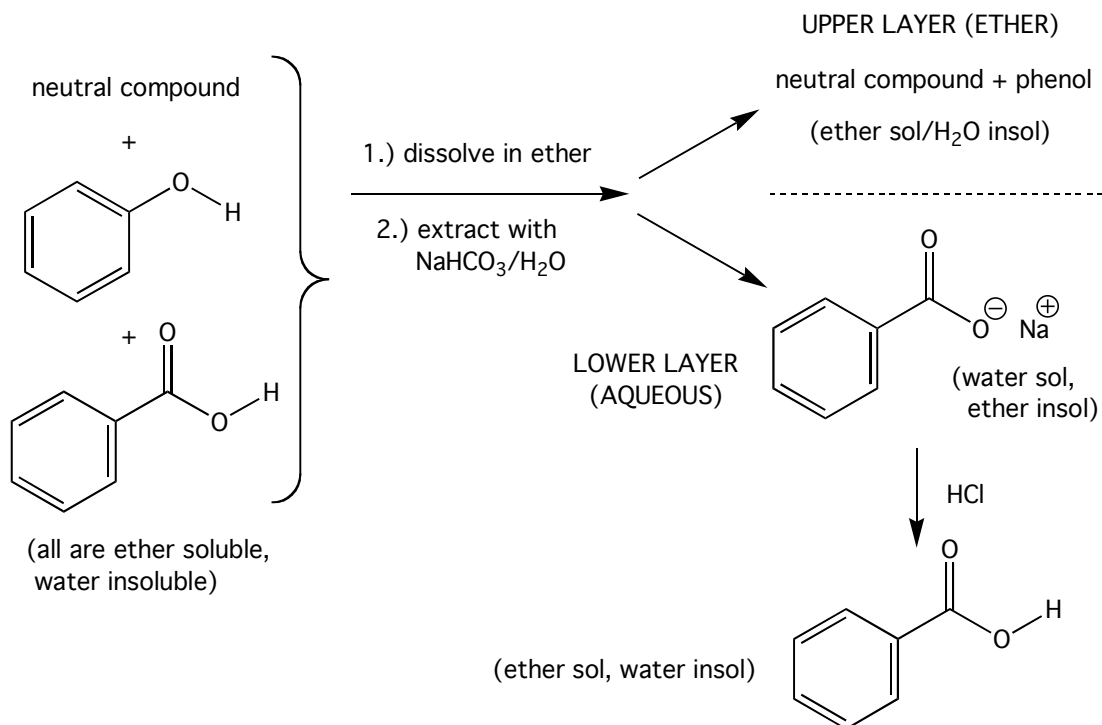
In the experiment done in this lab, a mixture of a carboxylic acid (stronger acid), a phenol (weaker acid), and a neutral compound will be separated by acid-base extractions. The separated compounds will be purified by recrystallization and identified by melting points. A general scheme for the separation is given below.

The mixture is dissolved in ether and mixed thoroughly with aqueous sodium bicarbonate (weaker base). After the layers settle, they are separated and placed into different tubes. The ether layer is then extracted with sodium hydroxide (stronger base), the layers separated, and each layer worked up separately. Three separate solutions result, one ether and two aqueous. Dissolved water is removed from the ether solution using a drying procedure and the ether is evaporated to yield the solid neutral compound. This can then be recrystallized to yield pure solid neutral compound.

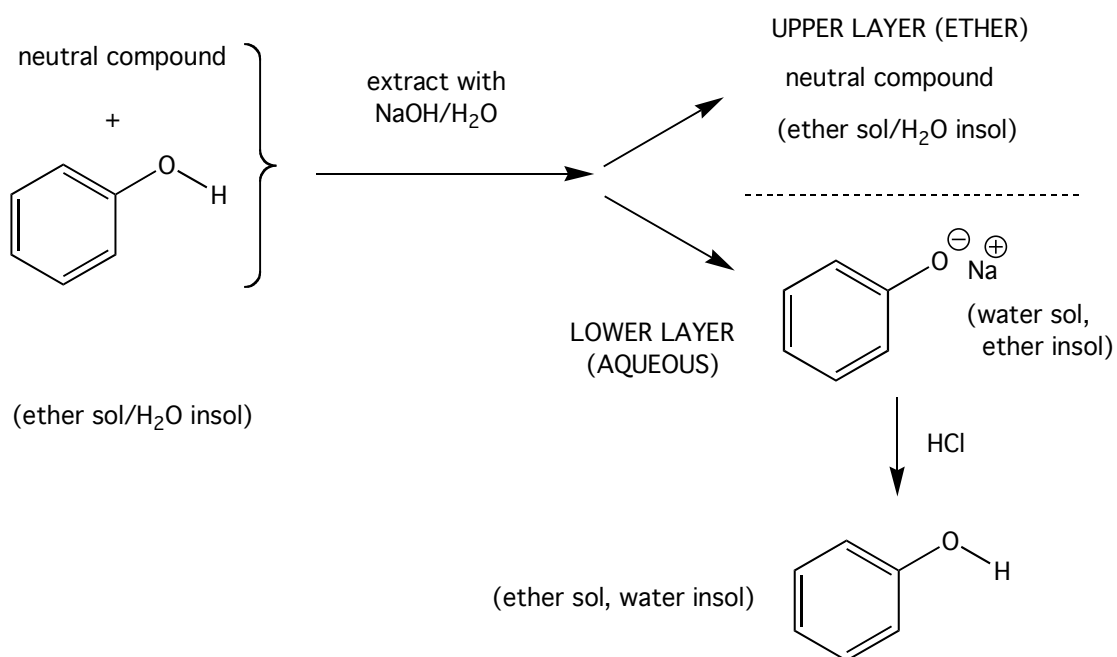
The basic aqueous solutions are neutralized with concentrated HCl to yield the carboxylic acid and phenol, which, because of their water insolubility, precipitate out. These can be collected, recrystallized and allowed to dry to yield pure carboxylic acid and pure phenol.

Note that the extractions must be done in the order shown, that is, first with sodium bicarbonate and then with sodium hydroxide. (What would happen if the sodium hydroxide extraction were done first?)

FIRST EXTRACTION



SECOND EXTRACTION



Neutralization of the carboxylic acid salt and excess sodium bicarbonate with concentrated hydrochloric acid. It is critical to add an amount of HCl necessary to completely neutralize the base, otherwise the yield of carboxylic acid will suffer. To be certain that neutralization is complete, a slight

excess of HCl is added. The amount of HCl needed is calculated as follows: 1.15 mL of saturated aqueous sodium bicarbonate is used in the extraction. This determines the amount of HCl needed. A saturated aqueous solution of sodium bicarbonate is 1 M (1 mole/liter). Concentrated HCl is 12 M. Because HCl reacts with sodium bicarbonate in a 1:1 molar ratio, it follows that 1 mL of saturated aqueous sodium bicarbonate would be neutralized with 1/12 mL of concentrated HCl. If 1.15 mL of sat'd aq sodium bicarbonate has to be neutralized, how much HCl is needed? First, how many moles of sodium bicarbonate is present in 1.15 mL of a sat'd aq solution?

$$1 \text{ mol/L} \times 0.00115 \text{ L} = 0.00115 \text{ mol (1.15 mmol) sodium bicarbonate}$$

Therefore, 0.00115 mol of HCl is needed for neutralization. How many mL of HCl then is needed?

$0.00115 \text{ mol} / 12 \text{ mol/L} = 0.000096 \text{ L} = 0.096 \text{ mL}$ or, rounded off, about 0.1 mL. Thus 1.15 mL of sat'd aq sodium bicarbonate is neutralized by about 0.1 mL of conc HCl. With our pipets, there are about 30 drops in one mL of conc HCl. This translates into about 3 drops of HCl, a very small amount indeed.

Drying the organic solvent. The organic solvent containing the neutral compound contains some dissolved water. If the solvent were evaporated at this point, the resulting solid neutral compound would be wet with water and would consequently be a gooey mess and would take a long time to dry. A drying procedure is therefore necessary to remove all traces of water before the solvent is evaporated. This procedure consists of two steps: (1) thoroughly mixing the solution with saturated aqueous sodium chloride (saturated salt solution) and discarding the aqueous layer (this is a preliminary drying step that removes most of the water) and (2), adding a solid inorganic drying agent (this strongly binds to the remaining traces of water dissolved in the organic solvent), allowing it to remain in contact with the solution for several minutes, then separating the solution from the solid drying agent. The solvent can then be removed by evaporation, leaving behind the solid neutral compound.

Very often in the synthesis of a compound or in the isolation of a compound from a natural source, acid-base extractions are used to either directly isolate a desired acidic or basic compound or to remove acidic or basic impurities. Extraction, along with recrystallization and distillation, is one of the most important separation and purification techniques in organic chemistry.