Chem 227 / Dr. Rusay

Separation and Identification of Unknown Compounds in a Mixture

Your challenge is less complicated than the pre-lab. There is no basic compound in the mixture.

One of the organic compounds in the mixture is a liquid in its pure state, b.p > 90 °C, and < 200 °C @ 1 atm; it does not contain nitrogen but has an oxygen containing chemical function other than a carboxylic acid. The other compound is a solid carboxylic acid and may contain additional functional groups. Both compounds are soluble in methyl-t-butyl ether but insoluble in water. Separate the compounds from each other, purify each compound, determine their respective spectroscopic and physical properties, and identify each.

General Guiding Principles:

Solubilities: Likes dissolve likes. Water / aqueous acid or aqueous base solutions and certain organic solvents are immiscible. Controlling the pH and mechanically manipulating immiscible liquid layers allow separation of mixtures of organic compounds, which have different types of chemical functions.

Solvents / Media:

Organic Solvents: dissolve most non-ionic compounds and most chemical functions.
Aqueous Base (5% sodium hydroxide): dissolves acidic chemical functions depending on relative strengths.
Aqueous Acid (5% HCl): dissolves basic chemical functions depending on relative strengths.
Water: dissolves ***charged*** stable species → ***ionic*** and ***highly polar*** compounds.

Classification of Chemical Functions (uncharged, non-ionic):

Acidic: carboxylic acids, phenols (generally dissolve in basic aqueous solution)
Basic: amines (generally dissolve in acidic aqueous solution)
Neutral: all other functions (generally soluble in organic solvents; relatively insoluble in water, aqueous base and aqueous acid);
Note: alcohols ionize with very strong, non-aqueous bases, eg $NaOCH_3$.

Salts: salts of organic functions dissolve in water (***charged species***)

Although both unknowns are generally soluble in methyl-t-butyl ether and insoluble in water, the acidic unknown is converted to a water-soluble, methyl-t-butyl ether-insoluble salt by neutralization with aqueous base (5% sodium hydroxide). The procedure involves the extraction of the acidic unknown from the methyl-t-butyl ether solution using aqueous base. Because t -butyl methyl ether and water are immiscible, separation of the two liquid layers can be carried out mechanically; the lower aqueous layer will contain the acidic unknown in the form of a water-soluble salt, and the upper methyl-t-butyl ether layer will contain the neutral compound. (Densities: H_20, d= 1.000 g/mL; t-BuOMe, d= 0.740 g/mL, b.p. ~55 °C).

Record the unknown's number in your notebook. Each unknown contains ~2 g of a solid carboxylic acid and ~10 mL of a neutral function compound. Using 5% NaOH and 5% HCl devise and draw a separation scheme, as in Question #4 of the prelab, and provide a procedure with a complimentary set of instructions that include the approximate amounts of reagents/solvents and instructions for filtration, drying, evaporation, etc.

A sample that is large enough to run an NMR neat (without solvent) of the neutral unknown is to be purified by simple distillation or through column chromatography using alumina. Determine the sample's b.p., refractive index, IR, and ^{1}H & ^{13}C NMRs. Send Dr. R. an e-mail indicating your unknown # with the unprocessed fid ^{1}H & ^{13}C NMR files included as attachments.

Determine the m.p. of the solid. If it has a range >4 ºC, purify the solid by recrystallization. Determine an appropriate solvent or mixed solvent pair. Carboxylic acids are rather polar, so for most samples a solvent like methanol, ethanol or water works well. Test a very small amount of the compound with the respective solvents. If these solvents do not work (too soluble), consult your lab textbook for recrystallization using a mixed solvent system.

Run ^{1}H & ^{13}C NMRs on the solid. The solid must be dissolved in a suitable solvent. Test its solubility in non-deuterated/ non-spectroscopic grade solvents first before using any NMR grade solvent. The solvent choices are carbon tetrachloride, chloroform, acetone, DMSO, and universal solvent. Have Dr. R. approve your selection before proceeding with NMR grade solvent.

Identify the respective compounds. Complete the form and turn in labeled samples of the 2 unknowns with your lab notebook pages attached.
