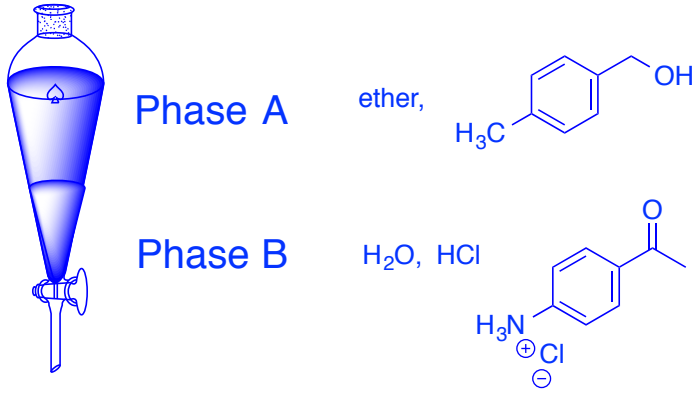
CHM2123 – Problem Set #1

1. In a beaker, you have a solution containing 50 mL ethyl ether, 3.1 g 4-amino acetophenone and 2.5 g 4-methylbenzyl alcohol. You are asked to add 50 mL H_2O to the beaker, along with five drops of concentrated HCl, and then to transfer the mixture to a 125 mL extraction funnel. Two phases appear in the extraction funnel. Indicate the contents of phase A and phase B *after* shaking. (**2 points**)



Water is more dense than ether, meaning that the aqueous phase will appear on the bottom.
Between the methyl, the benzyl alcohol, the ketone, and the amine, the amine represents a strong base, which will thus be protonated easiest. The cationic species is transferred to the polar, aqueous phase.

The neutral molecule remains in the neutral organic phase.

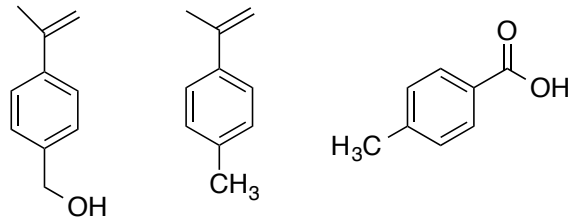
2. Why is Na_2CO_3 added to the tea mixture in step 5 of part A of this experiment? Justify your answer with a chemical equation. (**2 points**)

*Na_2CO_3, a good base, is **added to deprotonate** polyphenols, Ar-OH, found in tea, such as tannins, catechins and theaflavins. (**0.5 points**)*

$$Ar\text{-}OH + Na_2CO_3 \longrightarrow Ar\text{-}O^-Na^+ + Na^+HCO_3$$ ***(1 point)***

*Since caffeine is more basic than the polyphenols, they are resistant to deprotonation and remain neutral. Upon extraction with CH_2CL_2, **caffeine** is transferred to the **organic solvent** while the charged**, ionic species** reside in the polar, **aqueous phase**. (**0.5 point***

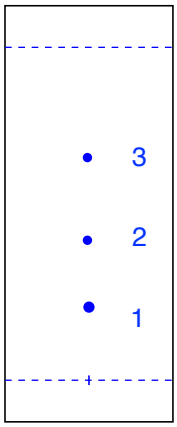
3. A dilute solution containing the following molecules is spotted onto a TLC plate. (**2 points**)



A **B** **C**

The plate was eluted with a mobile phase composed of 6:4 hexanes : ethyl acetate.

a) Calculate the R_f value for each spot.
b) Assign each compound to its corresponding spot onto the plate, and justify your reasoning.



B

A

C

Rf(B) = 2.3/3.5
= 0.67

Rf(A) = 1.4/3.5
= 0.4

Rf(C) = 0.8/3.5
= 0.23

*1 = C, a carboxylic acid is the **most polar** of the three and undergoes the greatest extent of **hydrogen bonding** with the stationary phase (silica gel) through both oxygens (as an acceptor) and hydrogen (as a donor), hence the smallest R_f value.*

2 = A, an alcohol is less polar than a carboxylic acid but more polar than a hydrocarbon. It also has decreased hydrogen bonding as it can only interact through the one oxygen and hydrogen.

3 = B, the hydrocarbon interacts the least with the stationary phase in the absence of heteroatoms, and is thus eluted furthest up the plate by the mobile phase.

1 point for assignment (0.5 if 1/3 correct)

0.5 points for explanations involving polarity

0.5 points for describing hydrogen bonding

4. From a mixture containing para-dichlorobenzene and benzil, you have isolated both compounds via liquid-liquid extraction to yield 0.2 g of para-dichlorobenzene and 1.9 g of benzil in the form of crude crystals. Between sublimation via a cold-finger and recrystallization with ethanol, select the best method for purification of each crude compound, and justify your answer. (**4 points**)
    a. para-dichlorobenzene
    b. benzil

a) Para-dichlorobenzene has a high vapour pressure, high volatility, and sublimes at near room temperature, making it particularly useful as a pesticide in mothballs and as a disinfectant in waste containers. The compound has a vapour pressure of 1.3 mmHg at 20˚C. The low quantity of crude also lends itself to a small-scale purification technique such as sublimation. Sublimation on a cold finger with dry ice would then be very easy.

b) Benzil, by contrast, has a low vapour pressure and would require significant temperature and vacuum to induce sublimation. It has a vapour pressure of 1.0 mmHg at 128˚C (and will be lower at 20˚C, for comparison to para-dichlorobenzene). The large quantity of crude crystals also lends itself easier to one round of recrystallization as opposed to multiple rounds of sublimation, having to remove crystals from the cold-finger each time.

Ethanol as a solvent, however, would not be particularly favourable for either compound for recrystallization, as both substances are soluble in ethanol at room temperature. To induce the purified crystals to crash out, the best approach would be to add a few mL of a more polar solvent to push the crystals to precipitate. H_2O would be a good choice, as both compounds are insoluble in water. As long as your co-solvent is miscible with your initial solvent, this technique will work.