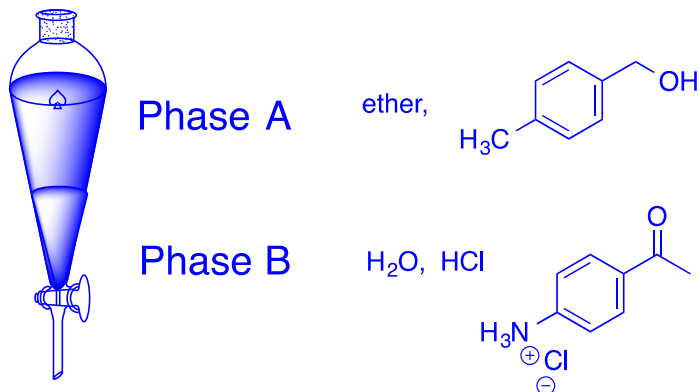


CHM2123 – Problem Set #1

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 H₂O 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.

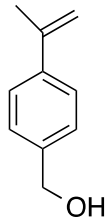
2. Why is Na₂CO₃ added to the tea mixture in step 5 of part A of this experiment? Justify your answer with a chemical equation. (2 points)

*Na₂CO₃, a good base, is **added to deprotonate** polyphenols, Ar-OH, found in tea, such as tannins, catechins and theaflavins. (0.5 points)*

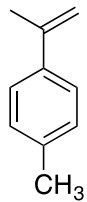


*Since caffeine is more basic than the polyphenols, they are resistant to deprotonation and remain neutral. Upon extraction with CH₂Cl₂, **caffeine** is transferred to the **organic solvent** while the charged, **ionic species** reside in the polar, **aqueous phase**. (0.5 point)*

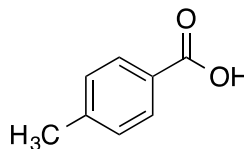
3. A dilute solution containing the following molecules is spotted onto a TLC plate. (2 points)



A



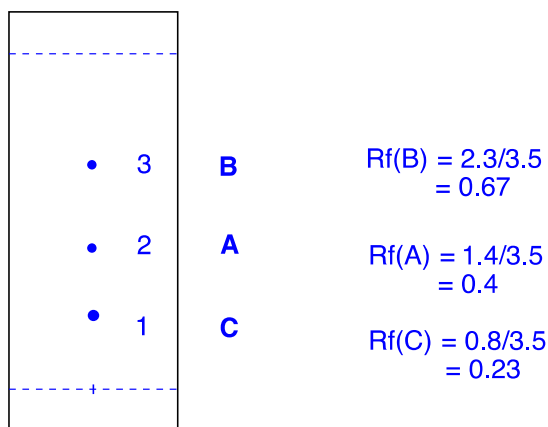
B



C

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

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



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. Do you hypothesize that violaxanthin, a carotenoid found in spinach, would have a smaller or larger R_f value relative to that of chlorophyll *a*? Explain your reasoning. (2 points)

*The R_f value of a compound is a function of its polarity and ability to hydrogen bond with the stationary phase, silica gel. A molecule's polarity is determined by the distribution of electron density within the molecule, or more specifically its dipole moment, where an imbalance of electron density gives rise to polarity. On the basis of polarity alone, the structure of chlorophyll *a*, with an electron-rich porphyrin ring and a long hydrocarbon handle, possesses a much stronger polarity relative to the symmetric violaxanthin, thus suggesting that chlorophyll *a* would have a lower R_f value. The presence of the hydroxyl groups on violaxanthin, however, impose strong polarity above the plane of the molecule and allow it to easily hydrogen bond with the silica gel. Accepting and donating of hydrogen through the alcohol groups render violaxanthin with a lower R_f value relative to that of chlorophyll *a*.*

5. a) When recrystallizing a compound from a crude product, explain why it is necessary to allow a mixture to cool to room temperature prior to placing it on ice. (1 point)

*Cooling the mixture slowly allows growing crystals to be in **equilibrium** with the saturated solution, and minimizes crystal lattice **impurities**.*

- b) After having dissolved the crude product in 10 mL ethanol, and following step 17 of Part A, you do not observe crystal formation in your beaker after 15 minutes. Provide an explanation. (1 point)

*There is **too much solvent** present, meaning that the solution is not saturated enough for crystal precipitation. (1 point)*

- c) What will you do to solve the problem? (1 point)

Evaporate off excess solvent on hotplate, and repeat step 17. (1 point)