

Exercise 10

Fig. X10-1

Solvents

Solvent selection is very important for many different techniques in organic chemistry. Recrystallization, extraction, chromatography and synthesis all critically depend on the right choice of solvent for optimal success. Some properties to seriously consider when selecting a solvent are solubility, boiling point, toxicity and cost (purchase price and disposal costs). Considering recrystallization as an example, the compound of interest should have low solubility in the cold solvent and substantial solubility in the hot solvent. The solvent should be relatively non-toxic and inexpensive and have low disposal hazards and cost. Its optimal boiling point should be in the range of about 60 - 90°C. The lower value affords a range between room temperature and the boiling point for increasing the solute solubility. Although not necessary, a boiling point below 100°C makes it possible to boil the solvent with a steam bath and it is easier to remove the solvent by rotary evaporation should that become necessary. For solvent properties, please refer to *Appendix B* or one of the Internet sites below:

<http://murov.info/orgsolvents.htm>

http://organicdivision.org/organic_solvents.html

<http://solvdb.ncms.org/solvdb.htm>

<http://www.alsnotebook.com/chlorformtraces.html> (nmr of common solvents)

http://www.wiredchemist.com/chemistry/data/physical_character_solvents.html

<http://www.cem.msu.edu/~reusch/OrgPage/tables.htm>

Knovel Critical Tables - Free registration required (on registration form,

http://www.knovel.com/web/portal/free_titles , or after clicking on

http://www.knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=761

select the Table for *Basic Physical Properties of Common Solvents* and register.



A partial view of Iguazu Falls on the border of Argentina and Brazil. Although water is commonly called the universal solvent, most organic compounds have limited solubility in water. Accordingly, water is seldom a good solvent for organic reactions but still finds extensive use in extractions. Water has many properties such as cost, toxicity and flammability that make water the solvent of choice when it has the desirable solubility properties.

1. Although benzene and carbon tetrachloride were commonly used as solvents a few decades ago, their use now is extremely limited and only as solvents of last resort? Why?
2. Although the use of carbon tetrachloride is strongly discouraged as a general solvent, it is still commonly used as solvent for nmr or ir spectroscopy. Why?
3. Select at least three solvents that could be used as solvents for determining ir spectra. Give advantages and disadvantages of each and discuss any possible advantages and disadvantages of using a deuterated form of the solvent.
4. Select at least three solvents that could be used as solvents for determining nmr spectra. Give advantages and disadvantages of each and discuss any possible advantages and disadvantages of using a deuterated form of the solvent.

5. Toluene is often used instead of benzene but its relatively high boiling point can be a disadvantage. Why?
6. Diethyl ether is still commonly used as a solvent but has several problems associated with its use. Explain these problems.
7. Dichloromethane (methylene dichloride) is also commonly used but has issues associated with its use. Explain these issues.
8. Water is often used to recrystallize carboxylic acids and other polar organic compounds that have a slight solubility in water. However, water has some disadvantages as a recrystallization solvent. What are the disadvantages?
9. Polar organic compounds often have very low solubility in the most commonly used organic solvents. This can present challenges. Name some of the polar organic solvents that could be considered as possible solvents for polar organic compounds.
10. Sometimes, it is desirable for the polar solvent to be aprotic. Suggest reasons for this and list the aprotic polar solvents from question #9.
11. Earlier questions discussed alternative solvents for use in IR and NMR spectroscopy. If a polar organic solvent is needed as a solvent for IR or NMR spectroscopy, what options are available?
12. Solvents like acetone and isopropyl alcohol are not useful for aqueous extractions. Why not?
13. In #12 you discussed one of the selection criteria for an extraction solvent. What other properties should be considered when choosing a solvent for the organic phase? Give reasons.
14. During an aqueous extraction, how do you know which phase is on the bottom?
15. Select at least five solvents that you would use as possible recrystallization solvents or possibly as elution solvents for column chromatography. Arrange them in terms of increasing polarity.
16. Is toxicity a special concern for any of the solvents listed in *Appendix B*?
- 17.¹ Solvent polarity is an important criteria to use for solvent selection. However, unlike a property such as boiling point, there is no simple method for measuring and reporting polarity. Dipole moments, dielectric constants and spectra shifts (used in *Appendix B*) are commonly used as a measure of polarity. Briefly discuss the issues associated with the ranking of solvent polarity.

¹Bonus Question