INTRODUCTION

This manual contains details of all the practical work you will be doing during the Chemistry 230 (Organic Chemistry) Course.

YOU ARE STRONGLY ADVISED TO READ THROUGH EACH LAB. WELL IN ADVANCE OF THE DAY OF THE PRACTICAL CLASS. STUDENTS WILL BE AT A DISADVANTAGE IF THEY HAVE NOT DONE ANY PREPARATION, AS SOME OF THE LABS. WILL NEED PLANNING BEFOREHAND IF THE WORK IS TO BE COMPLETED IN THE TIME AVAILABLE.

Attendance at practicals is compulsory. If you do not attend, your mark will automatically be zero, unless you present a medical certificate. (Medical certificates may be obtained from the campus nurse at no charge.) In some cases, if you act in good time, it may be possible to attend another section of the practical.

Make optimum use of your laboratory time. Some of the questions/follow-up work can be done later.

You should already be familiar with the laboratory safety rules, but take this opportunity to re-acquaint yourself with them.

Make sure you record all your observations, especially if you are working in a group.

The lists of apparatus and chemicals for each lab are intended primarily for use by the laboratory technicians, but you can use them to check that you have what is required, either on your table or on the front or side benches. If anything appears to be missing, let your lecturer know.

The total possible marks for the labs account for 20% of the total marks for the Chemistry 230 course.

If you find any errors, omissions, or parts of these sheets that are difficult to understand, please bring them to the attention of your lecturer.

SAFETY

A chemistry laboratory can and should be a safe place in which to work, provided that the correct precautions and safety procedures are followed.

The experiments you will be doing have been chosen in part because they involve little risk, if the instructions are followed carefully in the correct order. READ THE INSTRUCTIONS!

If an accident does occur, DO NOT PANIC. A minor accident may easily be turned into a serious one by over-reacting. If an accident happens to another student, tell them what to do, help them if necessary, and inform the lecturer. Clean up any spillages and/or breakages thoroughly. Ask the supervisor if in doubt as to what to do.

Safety Equipment.

Make careful note of the positions of the safety shower/eye-bath, fire extinguishers and fume cupboards, and know how to use them.

Eye protection.

Students must wear safety glasses at all times when in the laboratory (over your eyes, not up on your forehead/hair!). Each student must come to class with his or her own pair – available from Chapter One. It is not advisable to wear contact lenses in the laboratory.

Clothing.

Come to the laboratory in sensible clothing. Long flowing clothing is dangerous. Shorts and open shoes/sandals offer less protection than pants and regular shoes with non-slippery soles.. High heels are dangerous. Keep long hair tied back.

Working with Chemicals and Apparatus.

The following rules will help you to work in safety:-

1) Students must not work in the laboratory without the permission of a lecturer.
2) Follow instructions carefully.
3) Never smell or taste chemicals unless instructed to do so. Avoid breathing in fumes. Work in a fume cupboard if necessary, or if instructed to do so.
4) Avoid skin contact with chemicals. In the event of a spill, wash immediately under the tap, or use the shower or eye-wash if necessary.
5) Never eat or drink in the laboratory. Wash your hands before you leave.
6) Keep your work station tidy, and keep unneeded books etc. on the shelf, or in your bag, under the bench where nobody will trip over it.
7) Remain at your work station as much as possible. Do not wander around the laboratory unnecessarily.
8) NEVER heat substances in sealed test tubes or other sealed apparatus – they may explode. When heating substances in an open test tube, ensure the open end is pointing away from yourself and others.
9) Do not stand glassware near the edge of a sink or bench.
10) Take care when inserting glass tubing through stoppers. Use a cloth to protect your hands, and grip the tube near the end going into the hole. Do not over-tighten clamps on glassware. Avoid using cracked or chipped glassware.
11) Clean up all spillages or breakages immediately.
12) Do not dispose of flammable liquids down the sink.

General Laboratory Practice.

The following will help you, other students, the laboratory technicians, and your lecturer:-

1) Do not put insoluble solid waste into the sinks. Put it in the waste bin provided.
2) Report all breakages to the lecturer. You will not be charged, but it will help with re-stocking.
3) Please do not write on the benches. Writing is difficult to clean off.
4) Please leave the bench as you would wish to find it, even if it was less than perfect when you arrived!

PRACTICAL NUMBER 1
EXTRACTION: SEPARATION AND ISOLATION TECHNIQUES

INTRODUCTION

In this experiment you will separate the components of a mixture consisting of an acid, a base and a neutral substance by extraction. Extraction is a common technique used to separate a desired organic product from a reaction mixture or to isolate an organic substance from its natural source.

Extraction involves the use of two immiscible solvents which form two layers upon standing. Usually the solvents are water and an organic solvent. The desired substance (or a derivative of it) should be far more soluble in one solvent than in the other. When a mixture of substances is shaken with the two solvents, most of the desired substance (or its derivative) should dissolve in one of the solvents.

Although organic compounds are generally more soluble in an organic solvent than in water, many, especially those which can form hydrogen bonds, are partially soluble in water. They distribute themselves between the aqueous solvent and the organic solvent in proportion to their relative solubilities (S) in the two solvents.

The ratio of the concentrations (expressed in mass per unit volume of solvent e.g. g cm^{-3}) of a substance in the two solvents *at equilibrium* is an equilibrium constant, called its **distribution coefficient, K_D**:

$$K_D = \frac{S_o}{S_w} = \frac{C_o}{C_w}$$

where the subscript *o* stands for *oil* and *w* for *water*.

For example, suppose the solubility of compound A in ether and water is 0.30 g/100 cm^3 and 0.060 g/100 cm^3 respectively, then $K_D = \frac{0.30}{0.060} = 5.0$

In general, performing several extractions using smaller volumes of solvent is more efficient than performing a single extraction with a larger volume of solvent (see post lab question 1).

The extraction solvent

a) must be immiscible or sparingly soluble in the solvent from which the desired substance is to be extracted.
b) must readily dissolve the substance to be extracted and should extract only the desired substance or as small an amount as possible of any other substance present.
c) should not react chemically with the solute.
d) should have a low boiling point so it can be easily evaporated or distilled off from the desired solute after extraction. Common organic solvents used in extraction include ethoxyethane (diethyl ether or ether), petroleum ether[1] (a mixture of low-boiling alkanes), dichloromethane, trichloromethane (chloroform), and tetrachloromethane (carbon tetrachloride), ethyl ethanoate (ethyl acetate).

If chlorinated hydrocarbons are used, avoid breathing their vapours and getting them on the skin, because these compounds are **toxic** and some are **carcinogenic**.

Ethoxyethane (diethyl ether or ether) is highly flammable and, upon standing in air, its solutions may develop dangerous concentrations of explosive peroxides. **No flames must be in the lab when working with ethe**r. Furthermore, ether is slightly water-soluble (about 7g/100cm^3). However, because most organic compounds are highly soluble in it and because of its low boiling point (35°C), ether is frequently used.

Use of the separatory funnel

Extractions are usually performed with a separatory funnel. Your instructor will demonstrate the proper use of a separatory funnel.

[1] Often known as "pet ether".

Method

You will be provided with a mixture containing equal masses of m-nitroaniline (a base), benzoic acid (an acid), and naphthalene (a neutral substance) will be separated into its components by extraction.
Weigh out 1.5-2.0 g of the mixture and record the mass. Dissolve the mixture in 15 cm^3 of diethyl ether. Pour the solution into a 125°cm^3 separatory funnel. Extract three times with 15 cm^3 portions of 3 M HCl. Finally extract with 5 cm^3 water to remove excess HCl that may dissolve in the ether layer. Combine the three acid extracts with the water extract and set them aside.
Extract the remaining ether solution three times with 15°cm^3 portions of 10% aqueous NaOH and once with 5°cm^3 of water. Combine the alkaline and water extracts and set them aside.
Pour out the remaining ether solution through the top of the separatory funnel into a small Erlenmeyer flask. Add enough anhydrous calcium chloride to cover the bottom of the small Erlenmeyer flask, and swirl the mixture occasionally for 15°min. Decant the ether into a small beaker of known weight. Rinse the flask contents with a small amount (3cm^3) of ether, and add the rinsing to the beaker. Place the beaker in the hood to allow the ether to evaporate. Weigh the residue(X) and determine its melting point. Transfer the compound to a test tube labelled with the letter *X* and with your name and date. Cork it and submit it to your instructor.
Neutralize the combined acid extracts by adding 10% aqueous sodium hydroxide until the solution is alkaline to litmus paper. This is done by dipping a clean glass rod into the solution and then touching it to the litmus paper. Extract the alkaline solution twice with 15 cm^3 portions of ether. Combine both ether extracts. Add anhydrous calcium chloride, and swirl as described above. Decant the ether solution into a small beaker of known weight, rinse as described above, and place the beaker in the hood to allow the ether to evaporate. Weigh the residue (Y) and determine its melting point. Transfer the compound to a test tube labelled Y and with your name and date. Cork it and submit it to your instructor.
Neutralize the combined alkaline extracts by adding concentrated hydrochloric acid drop by drop until the solution is acid to litmus paper. Again, dip a clean glass rod in the solution and touch it to the litmus paper. The solution may be kept cool in an ice bath during neutralization. Recover the solid (Z) by vacuum filtration using a Buchner or Hirsch funnel, or by extraction with ether as described above. Allow the product to air dry, weigh it, and determine its melting point. Transfer the compound to a test tube labelled with the letter *Z* and with your name and date. Cork it and submit it to your instructor.
(Note that it is likely that some of the ether evaporated off during the extractions and may require replenishment.)
Calculate the percent recovery of each component.

Waste Disposal

Neutralize the basic and acidic aqueous filtrates with dilute hydrochloric acid and 10% aqueous sodium hydroxide, respectively, and pour into the aqueous waste container provided by your instructor.

Pre lab questions

1) Draw the structures of the three components of the mixture.
2) a) Write two equations (using structural formulae) for the reactions used in this experiment to separate and recover benzoic acid.
   b) Write two equations (using structural formulae) for the reactions used in this experiment to separate and recover m-nitroaniline.
3) Complete the table for the stated solvents.

Solvent	***Density/ gcm^{-3}***
Diethyl ether	
Dichloromethane (methylene chloride)	
Tetrachloromethane	
Ethyl ethanoate	

4) Complete the table.

Substance	*Melting Point/°C*
benzoic acid	
m-nitroaniline	
naphthalene	

5) Construct a flow chart to represent the separation of the three components of the mixture.

Post lab Questions

6) a) The distribution coefficient K_D for a compound, A, between diethyl ether and water is 5 i.e. $\frac{C_o}{C_w} = 5$, calculate the mass of A that is removed from a solution containing 50°mg of A in 50°cm^3 of water by extracting with 10°cm^3 of ether. (Hint. Let x°mg be the mass of A extracted into the ether layer).
7) b) Show that extraction twice with 50 cm^3 of diethyl ether instead of once with 100 cm^3 of diethyl ether would remove a larger mass of A from the water.
8) List three criteria that should be considered when selecting a solvent for extraction.
9) State two *advantages* and two *disadvantages* of using diethyl ether as an extraction solvent.
10) What is the practical advantage of using an organic solvent which is denser than water in an extraction?
11) Why must the stopper of the separatory funnel be removed before the liquid can be withdrawn through the stopcock?
12) a) Write two equations for the reactions used in this experiment to separate and recover benzoic acid.
13) b) Write two equations for the reactions used in this experiment to separate and recover *m*-nitroaniline.
14) Which of the components in the mixture was
    a) X?
    b) Y?
    c) Z?
15) Use the Henderson Hasselbalch equation to find
    a) the pH at which an aqueous solution would contain 10 times more benzoic acid molecules than benzoate ions.
    b) the pH at which an aqueous solution would contain 100 times more benzoic acid molecules than benzoate ions.
    c) the pH at which an aqueous solution would contain 10 times more benzoate ions than benzoic acid molecules.
    d) the pH at which an aqueous solution would contain 100 times more benzoate ions than benzoic acid molecules.
16) Phenol forms salts when treated with inorganic bases. However, phenol is a weaker acid than ethanoic acid. Aqueous sodium bicarbonate is usually alkaline enough to convert a carboxylic acid to its salt, but not alkaline enough to convert phenol to its sodium salt. Use this information to suggest an extraction procedure to separate phenol and ethanoic acid based on the information given.

Sources

Experiments for Introduction to Organic Chemistry, Bettelheim and Landesberg , Saunders College Publishing, 1997

Laboratory Manual, Organic Chemistry ... A Short Course Hart, Craine, Hart, Vinod 12th Ed, Houghton Mifflin, 2007