

# Experiment 5: Extraction, separation and the use of drying agents

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## Objectives

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This experiment is designed to

1. demonstrate how a solute can be extracted from one solvent to another.
2. show how a mixture of organic compounds can be separated into its components based on differences in acidity and basicity.
3. illustrate the use of a drying agent to remove traces of water from non-aqueous solutions.
4. introduce the concept of using a flow-chart to summarize laboratory procedures.

## Introduction to Extractions

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A method often employed to begin purification of an organic solid is a process called extraction. **Liquid-liquid extractions** takes advantage of the difference in solubility of a substance in two immiscible liquids. The two immiscible liquids used in an extraction process are (1) the solvent in which the solids are dissolved, and (2) the extracting solvent. The two immiscible liquids are then easily separated using a separatory funnel.

For example, to separate a mixture of an ionic compound, such as sodium chloride, and an organic, non-polar solid, such as anthracene,  $C_{14}H_{10}$ , extraction would be the method of choice. Ionic or polar materials are often quite soluble in water, while non-polar organic materials are normally more soluble in organic solvents than in water. Thus, in order to separate a mixture of sodium chloride and anthracene, the mixture is first dissolved in a mixture of water and an immiscible organic solvent, such as hexane. Two layers form, with the polar sodium chloride contained in the aqueous layer and the non-polar anthracene dissolved in the non-polar hexane. The mixture is then transferred to a separatory funnel and is shaken to ensure complete extraction of the two compounds into the appropriate layers. The layers are allowed to separate—in this instance, the organic layer will be on top, because the density of hexane is  $0.66 \text{ g} \cdot \text{mL}^{-1}$  and that of  $H_2O$  is  $0.99 \text{ g} \cdot \text{mL}^{-1}$ . The lower layer is drained out through the stopcock, and the upper layer is poured out through the top of the funnel. In principle, we have only to boil off the water to get the sodium chloride and evaporate the hexane to get the anthracene, and we have successfully

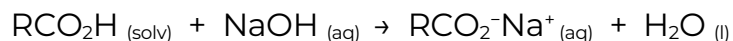
separated the mixture. However, to remove the last traces of impurities, the hexane layer would be washed by adding a little fresh water, shaking and draining off the aqueous layer. Similarly, the combined aqueous layers would be re-extracted with a little fresh hexane to remove the last of the anthracene.

Your task in this experiment is to isolate, purify and identify the compounds present in a three-component mixture. The mixture will consist of an organic acid (benzoic acid, 2-methylbenzoic acid, 4-methylbenzoic acid, 4-chlorobenzoic acid, or salicylic acid), an organic base (3-nitroaniline or 4-chloroaniline) and a neutral hydrocarbon (naphthalene).

An example as to when separations are used is during the Cannizzaro reaction where you are required to separate an organic acid from a neutral alcohol. In fact, most organic syntheses involve performing an extraction/separation at some point, if only to extract the desired organic compound from the reaction mixture. The organic acid and base will be purified by recrystallization, thereby providing you further practice in this important technique. The naphthalene will be purified by sublimation. The unknown compounds will be identified through use of the mixed melting point technique that was introduced in Experiment 1.

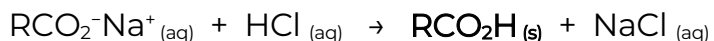
### Separation of the Organic Acid

The three compounds in your mixture are all virtually insoluble in water. However, they are soluble in dichloromethane (also called methylene chloride), an organic solvent which is immiscible in water. You will begin the experiment by dissolving the mixture in dichloromethane and adding aqueous sodium hydroxide to the solution. As water and dichloromethane are immiscible, two layers will form. The dilute inorganic base, sodium hydroxide, reacts with the organic acid, HA, to produce a water-soluble salt,  $\text{RCO}_2^-\text{Na}^+$ :



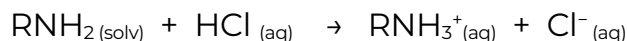
### Recovery and Isolation of the Organic Acid

Thus, the organic acid (in the form of its sodium salt) is extracted from the dichloromethane layer into the aqueous layer. The neutral hydrocarbon and the organic base are unaffected and remain dissolved in the dichloromethane. The two layers are separated, and each layer is washed: the aqueous layer with dichloromethane, the organic layer with aqueous base. The washings are then combined with the appropriate layers. To recover the organic acid or base, strong acid or base is added respectively. When strong acid is added to an aqueous solution containing the salt of an organic acid, the organic acid precipitates from solution (which then can be isolated by suction filtration):



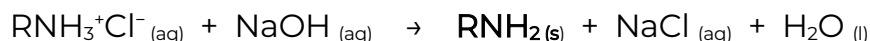
## Separation of the Organic Base

To this point, only one of the three components has been isolated and we still have a mixture of a neutral hydrocarbon and an organic base dissolved in dichloromethane. If dilute inorganic hydrochloric acid is added, it reacts with an organic base,  $\text{RNH}_2$ , to produce a water-soluble salt,  $\text{RNH}_3^+\text{Cl}^-$ , two layers again form and the organic base is extracted into the aqueous layer as its conjugate acid:



## Recovery and Isolation of the Organic Base

When strong base is added an aqueous solution containing the salt of an organic base, the organic base precipitates from solution (which then can be isolated by suction filtration):



The two layers are then separated and washed as described above. The organic base can now be isolated by filtration, purified, and identified.

The final task is to obtain the neutral hydrocarbon from the dichloromethane solution. Although one might think that simply evaporating the solvent would yield the desired product, the solution needs to be dried before this operation is performed. Despite the assumptions made previously, dichloromethane and water are not totally immiscible, and the small amount of water that is dissolved in the dichloromethane needs to be removed before an attempt is made to isolate the neutral hydrocarbon.

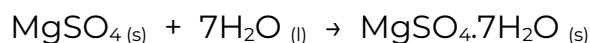
Small amounts of water can be removed from an organic solvent by allowing the solvent to stand over a drying agent in a closed vessel. The drying agent is then usually removed by filtration. Some commonly used drying agents are described below. Once the organic solution has been dried and the drying agent removed, the dichloromethane can be removed, using a rotary evaporator (Figure 5.1), and the neutral hydrocarbon can be purified, in this experiment by sublimation.

## Drying agents

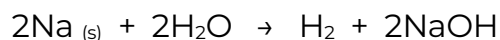
There are two main types of drying agents: (1) those used to dry wet solvents saturated with water (1-6 below), and (2) those used for solvents containing very little water (7-9 below).

|   | Drying Agent (anhydrous)           | Capacity/Efficiency : | Drying Compatibility  |
|---|------------------------------------|-----------------------|---|
| 1 | calcium chloride                   | large/low             | not good for alcohols, amines, phenols  |
| 2 | potassium carbonate                | fair/fair             | not good for acidic materials   |
| 3 | disodium sulfate                   | large/ slow and low   | good with organic solvents  |
| 4 | magnesium sulfate                  | large/good and rapid  | good with organic solvents  |
| 5 | calcium sulfate                    | large/good            | good with organic solvents  |
| 6 | potassium hydroxide                | large/v.g. and rapid  | good for amines   |
| 7 | sodium metal                       | small/v.g and v.fast  | not good with acidic protons, halocarbons (violent reactions).  |
| 8 | phosphorous pentoxide              | small/v.g and v.fast  | good only for relatively dry solvents, not good with alcohols, ketones, amines or acids   |
| 9 | metal hydrides (CaH <sub>2</sub> ) | small/v.g and v.fast  | good only for relatively dry solvents, not good for cmpds. with acidic H, C-hetero-atom, double bonds, or chlorocarbons (violent reactions) |

Type 1 drying agents are anhydrous salts, and act by combining with water in the organic solvent to form a hydrated salt which is insoluble in the solvent and can be removed by filtration. Example of Type 1 drying agent reaction with water:



Type 2 drying agents work because they react with any water present in the organic solvent. For example,



Often such reactions are violent, and consequently these drying agents are only used on solvents which are known to contain only a very small amount of water.

It is poor technique to use an unnecessarily large quantity of drying agent when drying a liquid, as the desiccant may adsorb or absorb the organic liquid along with water. Also, mechanical losses on filtration of the dried solution may become significant. The amount of drying agent required will depend on the quantity of water present and on the drying capacity of the desiccant. In general, a portion of drying agent that covers the bottom of the vessel containing the liquid should suffice. If additional desiccant is needed, more can be added.

As many hydrates lose their water when heated, it is important that the drying agent be removed by gravity filtration (or by decantation) before any distillation is attempted.

**Note:** To dry an organic solid, vacuum drying is used to remove unwanted moisture. This is because most organic solids will oxidize or decompose if heated.

## Summary of Liquid-Liquid Extraction Procedure

Remember there are essentially five steps to performing a extraction using a separatory funnel.

1. Dissolve the unknown compound in a solvent. Place the mixture in the separatory funnel supported with a ring clamp on a retort stand.
2. Add the extraction solvent to the separatory funnel.
3. Stopper the funnel, invert the funnel, vent, shake gently and vent again. Continue shaking/venting until no further pressure is released and then gently shake the funnel for 30 sec.
4. Return the separatory funnel to the ring clamp and allow the layers to separate.
5. Remove the stopper, drain the lower layer through the stopcock (out the bottom). Remove the upper layer by pouring it out of the top of the separatory funnel.