Experiment 5: Extraction

Introduction: In synthesis, the desired product must be separated from the by-products, excess reactants, impurities, and other substances that may be present in the reaction mixture. Similarly, substances in nature are always mixed with other substances. Extraction is the most common technique used to separate a desired organic product from a reaction mixture or to isolate an organic substance from its natural source. Extraction usually involves shaking a solution that contains the desired substance with an immiscible solvent in which the desired substance is more soluble than it is in the starting solution. Upon standing, the solvents form two layers that can be separated. Extraction may have to be repeated several times to effect complete separation.

Most commonly, one of the solvents is organic and the other aqueous. Inorganic compounds can usually be separated from organic compounds in this way since the former dissolve in the aqueous phase and the latter dissolve in the organic solvent. In such cases, a single extraction may suffice to effect satisfactory separation.

When choosing a solvent, many properties must be considered. The extraction solvent must readily dissolve the substance to be extracted, yet it must be only sparing soluble in the solvent from which the desired substance is to be extracted. Also, it should only extract the desired substance or as small an amount as possible of any other substance present. It should not react chemically with the solute in any undesirable way and it should be easily separated from the desired solute after extraction. This last requirement can be met if the solvent is low-boiling and easily removed by distillation.

Common organic solvents that fulfill these requirements include many hydrocarbons and their chloro derivatives, such as benzene, petroleum ether (a mixture of low-boiling alkanes), dichloromethane, chloroform, and carbon tetrachloride. If benzene or chlorinated hydrocarbons are used, however, it is important to avoid breathing their vapors because these compounds are toxic and some are carcinogenic. They can be used safely if we carry out operations in an efficient fume hood and take care to avoid getting them on the skin. Diethyl ether (usually referred to as ether) is highly flammable and, upon standing in air, its solutions may develop dangerous concentrations of explosive peroxides. Furthermore, it is slightly water-soluble. Nevertheless, because most organic compounds are highly soluble in it and because of its low boiling point, ether is frequently used despite its drawbacks.

Sometimes we can use desirable, easily reversed chemical reactions such as acid-base reactions to effect separation by extraction. For example, dilute sodium hydroxide converts organic acids to their sodium salts:

$$RCO_2H + Na^+OH^- \rightarrow RCO_2^-Na^+ + H_2O$$

Although a particular acid may not be soluble in water, its more polar sodium salt usually is. When a mixture of a neutral compound and an acidic, water-insoluble compound in an organic solvent is shaken with dilute aqueous sodium hydroxide, the acid is converted to its sodium salt, which dissolves in the aqueous layer, and the neutral compound remains in the organic layer. After the layers are separated, the acid is recovered by acidifying the aqueous layer with a strong acid:

$$RCO_2^-Na^+ + HCl \rightarrow RCO_2H + NaCl$$

Dilute aqueous acid can be used to extract basic compounds, particularly amines, from neutral or acidic substances by converting them to water-soluble alkylammonium slats:

$$RNH_2 + H^+Cl^- \rightarrow RNH_3^+Cl^-$$

After separating the organic and aqueous layers, we can recover the amine from the aqueous layer by making the solution alkaline with a strong base:

$$RNH_3^+Cl^- + NaOH \rightarrow RNH_2 + H_2O + NaCl$$

Extractions are usually performed with a separatory funnel. Improperly handled, this moderately expensive piece of glassware is easily broken. When using one, follow these steps:

1. Support the funnel in an iron ring attached to a ring stand (see figure 1).
2. Close the stopcock and add the liquids to be separated.
3. Insert the stopper, lift it out of the ring, and invert the funnel holding the stopper with one hand and the stopcock with the other (see figure 2).
4. With the barrel pointing away from everybody, slowly open the stopcock. This will relieve any pressure build-up.
5. After the pressure is released, close the stopcock, shake the funnel gently two or three times, and again relive the pressure. Repeat this two or three times.
6. Replace the funnel in the iron ring and remove the stopper immediately. Allow the funnel to stand until the layers separate.
7. Slowly draw off the lower layer through the stopcock into a flask or beaker of the appropriate size. Close the stopcock when the upper layer enters the stopcock bore.
8. Pour the upper layer out through the top of the funnel.

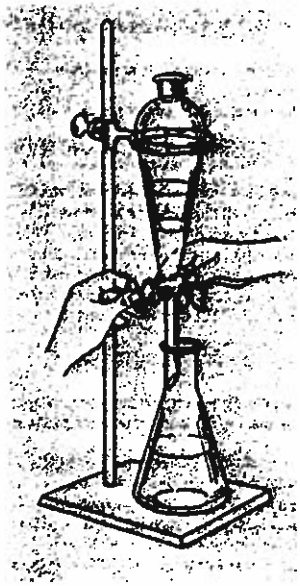

Figure 1

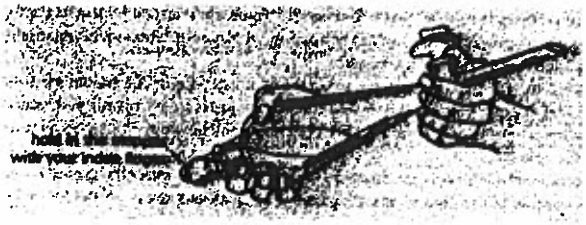

Figure 2

Sometimes, it is difficult to obtain a sharp separation of layers because an emulsion has formed. Gentle swirling of the funnel in an upright position, gentle stirring with a glass stirring rod, and addition of salt to the aqueous layer may overcome this difficulty.

In this experiment, a mixture of benzoic acid and naphthalene (a neutral substance) will be separated into its components by extraction.