Experiment 3: Distillation

Objectives

This experiment is designed to:

1.   demonstrate how a liquid may be purified by simple distillation and its boiling point determined during the process.

2.   illustrate how two liquids can be separated by fractional distillation.

Introduction to Distillation

Just as recrystallization is used to purify an organic solid, distillation is used to purify an organic liquid compound. There are three major reasons why we might have to distill an organic liquid compound:

1.   the compound may need to be purified prior to use in an organic synthesis,

2.   to assist in characterization if the compound is new or unknown,

3.   the organic compound must be highly pure before it can be administered medically.

In the previous two experiments, we learned that we can increase the purity of a solid compound by recrystallization, and we can check its purity by measuring the melting point. In general, a sharp melting point suggests a pure compound.

An impure liquid can be purified by distillation. Distillation is probably the most important purification technique for organic liquids. It involves heating a liquid to its boiling point at atmospheric or reduced pressure to convert it to its vapour and then condensing the vapour back to the liquid by cooling. A pure liquid compound will have a sharp and narrow boiling point range, while an impure liquid compound has a broad and depressed boiling point. Also, a pure liquid will have a very specific refractive index (see Exp. 4). A comparison of the refractive index (n) with literature values gives an indication of the liquid's purity.

The boiling point of a liquid is that temperature at which the vapour pressure (escaping tendency) of the liquid equals the atmospheric or applied pressure; that is, when liquid and vapour are in equilibrium. Thus, if you decrease the applied pressure by evacuating the system, you decrease the boiling point of the liquid. Similarly, pressurizing the system increases the boiling point. In *Chemistry 350* you will carry out all your distillations at atmospheric pressure and will not be concerned with **vacuum distillation**. However, you will be able to observe the effect that reducing the pressure has on the boiling point of a liquid when you use the rotary evaporator later in the course.

A homogenous mixture (i.e., a solution) of two liquids boils when the vapour pressure of the mixture is equal to the applied pressure, that is, when the sum of the partial pressures of the components (P_A, P_B, P_C ...) equals the applied pressure, P. Thus, at the boiling point

$$P = P_A + P_B + P_C \ ...$$

For those solutions which are "ideal", the partial pressure of each of the components present in the solution is given by Raoult's Law.[1] This law states that the partial pressure of component A, P_A, at any given temperature, is equal to the vapour pressure of the pure substance at that temperature, P°_A, multiplied by the mole fraction of that substance present in the solution, X_A. Thus,

$$P_A = P^{\circ}_A X_A$$

$$P_B = P^{\circ}_B X_B$$

and so on.

By combining the mathematical relationships expressed to this point, we see that

$$P = P^{\circ}_A X_A + P^{\circ}_B X_B \ ...$$

When a homogenous mixture of two liquids begins to boil, the composition of the vapour depends on the ratio of the partial pressures of the components present. Because the vapour pressure of the lower boiling component is higher than that of a higher boiling component, the vapour will be "enriched" in the lower boiling point component when compared with the liquid mixture. As the

[1] Francois Raoult in 1886 said "ideal solutions are characterized by the weighted averages of the properties of the components."

distillation proceeds, the mixture becomes depleted of the lower boiling component. Thus, the boiling point rises and a greater mole fraction of the higher boiling component appears in the distillate.

Figure 3.1 shows that a mixture consisting of 80 mol % B and 20 mol % A (i.e., a mixture in which the mole fraction of B is 0.80 and the mole fraction of A is 0.20) will boil at temperature T_1. The vapour composition curve shows that the composition of the vapour obtained at this temperature is 50% A and 50% B. If this vapour is condensed and redistilled, its boiling point would be T_2 and the vapour obtained would consist of 80% A and 20% B. Of course, this analysis is highly theoretical: in practice we have a dynamic situation that is constantly changing. For example, as soon as the first few drops of distillate are collected from boiling the original mixture, the mixture becomes depleted of the lower-boiling component (A) and its boiling point rises. However, in theory at least, one should be able to separate a mixture of two liquids into its components by carrying out a series of simple distillations as described above. In practice, the same result can be achieved using a process called **fractional distillation**.
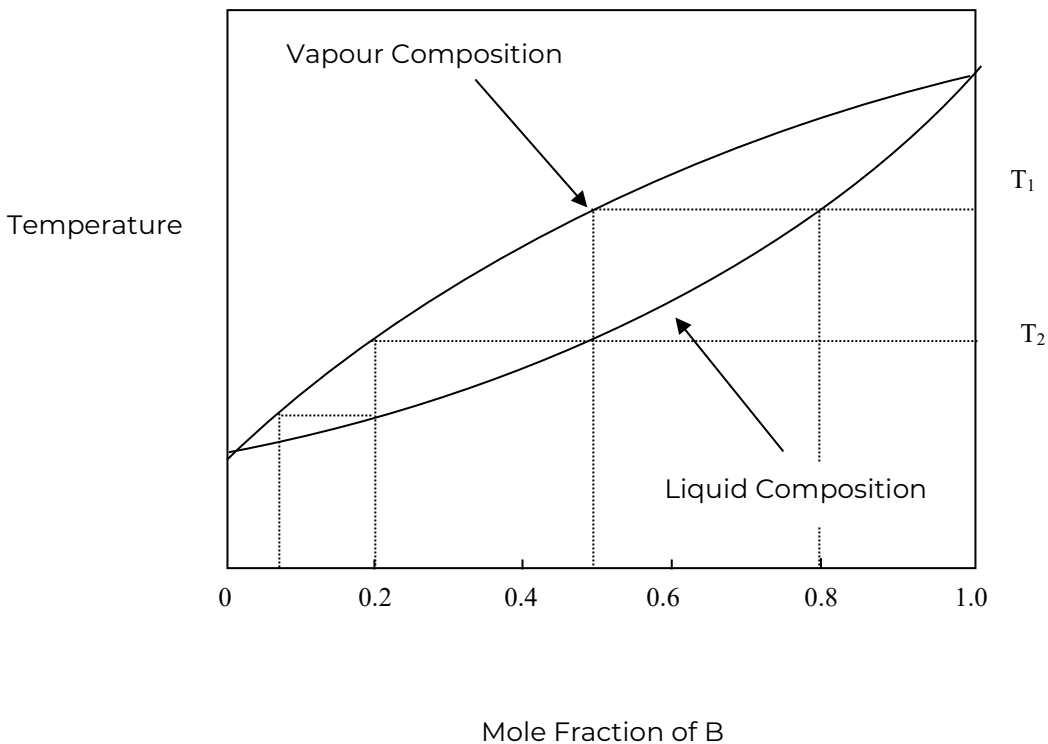
Figure 3.1. Temperature-composition diagram for an ideal two-component mixture.

A comparison of the setups used in simple and fractional distillations (Figure 3.2) reveals that the only difference between the two is the inclusion of a **fractionating** column in the latter. The purpose of this column is to enable the vapour to condense and evaporate a number of times as it rises up from the distillation flask to the still head. Thus, performing a fractional distillation is equivalent to carrying out a series of simple distillations along the lines suggested above. A good fractionating column can often produce a distillate that is comparable to the product that would be obtained from 25-100 successive simple distillations. Thus, the efficiency of a column is sometimes expressed in terms of its number of **theoretical plates**, where each plate corresponds to one simple distillation. Although it might appear that the more theoretical plates a column has the more efficient it would be, it has to be remembered that the more plates there are, the greater the volume of liquid that is retained on the column and cannot be distilled; that is, the greater the

column holdup. It is impossible to distill a sample whose volume is less than the volume of the column holdup.
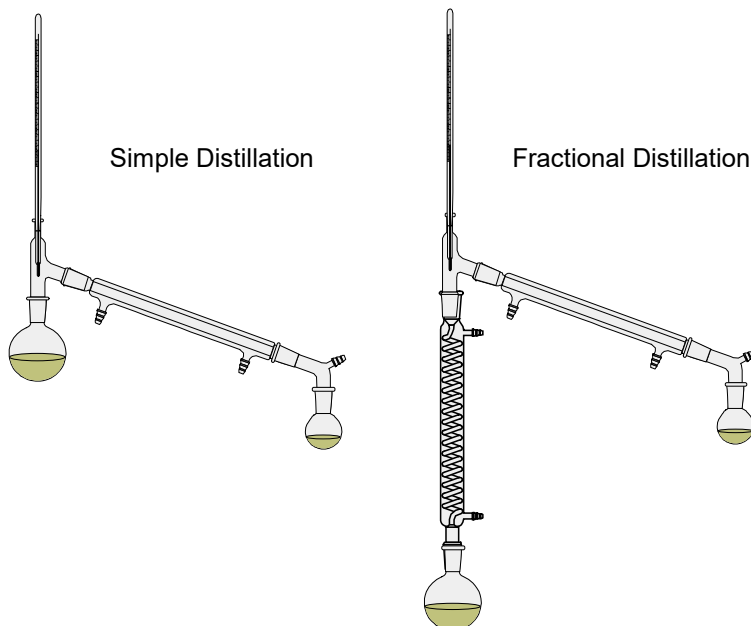

Figure 3.2. Simple and fractional distillation set-ups.

Some other terms that are encountered in discussions of fractional distillation include: **height equivalent to one theoretical plate** (HETP), which is the length of column that corresponds to one simple distillation; **throughput**, the maximum volume of distillate that can be obtained per unit time while still maintaining equilibrium throughout the column; and the **reflux ratio**, the ratio of the volume of condensate formed at the top of the column and returned to the system to the volume removed as distillate, that is

$$\text{Reflux ratio, R} = \frac{\text{volume of condensate returned to the column}}{\text{volume of condensate removed as distillate}}$$

An ideal column has a high number of theoretical plates, a low holdup, and a high throughput, and maintains its efficiency even at low reflux ratios. A glass tube packed with stainless steel sponge, which is the type of column you will be using, typically has a throughput of 2-5 mL· min^{-1}, an HETP of about 4 cm, and a holdup of 1-5 mL· plate^{-1}.

To this point, our discussion has been concerned with "ideal" solutions. "Real" solutions often have a particular composition for which the vapour and the liquid have an identical composition. Such a mixture is called an **azeotrope** (or **azeotropic mixture**), and the separation of such a mixture into its components cannot be achieved by means of a distillation, simple or fractional. A phase diagram for the ethanol-benzene system is shown in Figure 3.3. Notice that a low-boiling azeotrope (b.p. 68.2° C) is formed by a solution containing 45.1 mol % ethanol and 54.9 mol % benzene.
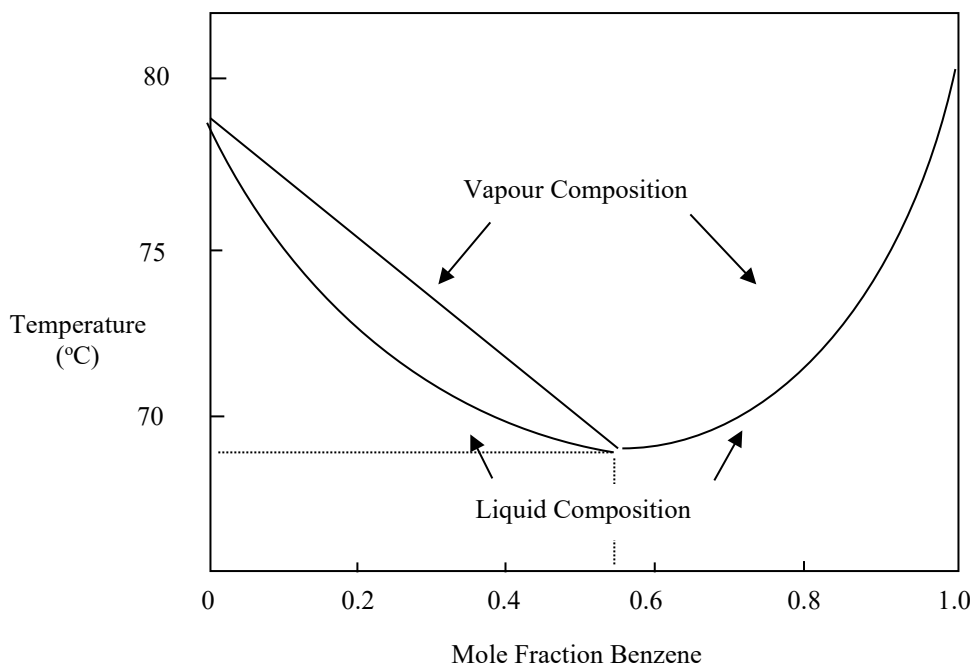

Figure 3.3. Temperature-composition diagram for a mixture of ethanol and benzene.

Background Information

In Part A of this experiment, you will be given an impure sample of cyclohexanol (contaminated with toluene (soluble impurity)). You will remove the contaminating toluene first (called the 'forerun'), then collect a second fraction containing 'purified' cyclohexanol.

cyclohexanol   cyclohexane   toluene
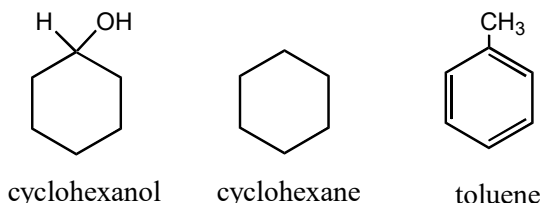
In Part B of this experiment, you will be given a 1:1 mixture of cyclohexane and toluene. You will fractionally distill the mixture, collecting first mainly the cyclohexane (fraction 1), then you will collect an intermediate second fraction containing both cyclohexane and toluene, and finally a third fraction containing mainly toluene.

Important: The boiling point of a liquid is defined as the temperature at which the atmospheric pressure and the vapour pressure of the liquid are equal. Thus, the boiling point of a liquid is pressure dependent. (e.g., the lower the atmospheric pressure the lower the boiling point or the higher the elevation the lower the boiling point). For a more precise correction of the boiling point, it is necessary to know the atmospheric pressure (in mmHg), **A.P**, at the time and location where the boiling point, **B.P. obs,** is measured. The corrected boiling point, **B.P. 760 mmHg**, can be calculated from the formula:

B.P. 760 mmHg = B.P. obs – 0.05 (A.P. mmHg – 760 mmHg)

Where:

B.P. 760 mmHg = normal boiling point (calculated)

B.P. obs = observed boiling point (measured)

A.P. = observed atmospheric pressure (mmHg)

As a general rule, boiling points will change about 0.5 °C for each 10 mmHg change in atmospheric pressure from 760 mmHg. In Edmonton, it is thus normal for boiling points to be approximately 3 °C lower than they would be at sea level.