**Liquid Vapor Equilibrium (LV)**

**Objective**

The purpose of this experiment is to obtain the liquid-vapor phase diagram for methanol-ethyl acetate mixtures and to use this diagram to determine the boiling point and composition of the azeotropic mixture.

**Caution**

The liquids you are using are flammable. Watch out for burns. The still is very fragile. Do not use boiling chips. Check constantly for an adequate flow of water through the condenser. The water pressure in the lab fluctuates tremendously, and a high flow rate may cause the rubber hose to burst. Do not turn the water flow up too high. A regular but steady stream is adequate. Check the water flow periodically to make sure you have a slow but regular water flow.

Left over chemicals should be placed in appropriate marked waste bottle in hood.

Do not wipe the glass surface of the refractometer. Allow it to air dry or if necessary blot gently with Kipwipe, but do not wipe as it may scratch glass surface.

When you are done with experiment remove glass stopcock from distillation set up and place on paper towel on the bench next to distillation apparatus. If stopcock is left in the device as it cools the stopcock will become stuck and it is very hard to remove. DO NOT leave stopcock in distillation apparatus.

**Theory**

When a mixture of liquids is boiled the composition of the vapor phase is usually different than the liquid phase. For some mixtures there is one unique composition where the liquid and vapor phases are identical. A mixture of this special composition is called an azeotrope. The azeotrope may have a boiling point higher than the boiling point of the two pure liquids from which it is made (maximum boiling point azeotrope). The azeotrope may have a boiling point lower than the boiling point of the two pure liquids from which it is made (minimum boiling point azeotrope). A maximum boiling point azeotrope might be expect in a mixture where the intermolecular forces between different A and B molecules are stronger than the forces between either of the pure (A and A) or (B and B) forces. A minimum boiling point azeotrope might be
expect in a mixture where the intermolecular forces between different A and B molecules are weaker than the forces between either of the pure (A and A) or (B and B) forces.

Read pages 182 – 184 in Physical Chemistry 8th edition by Atkins and de Paula for background information about temperature–composition phase diagrams and for examples of different types of azeotropes. Be sure to look at sample phase diagram for minimum boiling point azeotrope before you make plot with your own data.

Procedure Instructions

This experiment is performed using a Choppin-Cottrell boiling point apparatus. One end of the 3-way stopcock has been painted red (see Figure 1). In order to return the condensed vapor to the still, the stopcock should be in position (1), Red Up. In order to obtain a sample of the condensed vapor, the stopcock should be in position (2), Red Down. In order to obtain a sample of the liquid in the still the stopcock should be in position (3), Red Left.

Part I

First rinse the still with 10 mL of methanol by pouring the liquid down the condenser using a funnel. Then drain the liquid out the spigot. Tip the ring stand a little in order to get all of the liquid out. Now add 50 mL of methanol and begin heating. The variac power transformer will need to be at its highest setting, 140. Place an empty beaker under the spigot to catch any leaks. When you are turning the 3-way stopcock, gently push in on it to keep it tightly seated. After boiling enough for the thermometer to come to a steady value, record the boiling point of the pure methanol. When boiling the pure methanol, you do not determine the refractive index, but assume the liquid and vapor are 100 percent pure.

Add 5 mL of ethyl acetate to the methanol already in the apparatus and continue boiling. Again wait until the thermometer is at a steady value. Allow the system to reach equilibrium and measure the boiling point of the new mixture.

Collect a small sample of the condensed vapor and a small sample of the liquid in marked vials. When you collect a sample, you may need to discard the first liquid that comes out of the spigot because previous liquid tends to remain in the spigot. Allow the samples in the vials to cool to room temperature prior to determine the refractive index of the liquid sample and the condensed vapor sample.
Each pair of these vials provide two data points on your graph that share the same boiling point temperature, but represent the liquid and vapor composition. You will repeat this procedure every time you have a different composition of liquid mixture in your boiling point apparatus.

Add another 5 mL of ethyl acetate and repeat the above procedure. Then add 10mL amounts repeating the above measuring procedure until the total volume is about 50mL of methanol and 40mL of ethyl acetate. The sequence of ethyl acetate volumes added is 5, 5, 10, 10, and 10 mL.

Turn off and lower the heating mantle and allow the still to cool. Drain the liquid.

Part II

First rinse the still with 10 mL of ethyl acetate by pouring the liquid down the condenser using a funnel. Then drain the liquid out the spigot. Carefully tip the ring stand a little in order to get all of this liquid out. Now add 50 mL of ethyl acetate and begin heating. The variac power transformer will need to be at its highest setting, 140. Place an empty beaker under the spigot to catch any leaks. When you are turning the 3-way stopcock, gently push in on it to keep it tightly seated. After boiling enough for the thermometer to come to a steady value, record the boiling point of the pure ethyl acetate. When boiling the pure ethyl acetate you do not determine the refractive index, but assume the liquid and vapor are 100 percent pure.

Repeat procedure used previously but now the ethyl acetate is the starting liquid and incremental amounts of methanol. First add 2 mL of methanol and wait until the thermometer is at a steady value. Allow the system to reach equilibrium and measure the boiling point of the new mixture. Collect a small sample of the condensed vapor and a small sample of the liquid in marked vials. When you collect a sample, you need to discard the first liquid that comes out of the spigot because previous liquid tends to remain in the spigot. Allow the samples in the vials to cool to room temperature prior to determine the refractive index of the liquid sample and the condensed vapor sample.
Each pair of these vials provide two data points on your graph that share the same boiling point temperature, but represent the liquid and vapor composition. You will repeat this procedure every time you have a different composition of liquid mixture in your boiling point apparatus. Add 3mL of methanol and repeat the above measuring procedure. The total volume is 80mL of ethyl acetate and methanol. The sequence of volumes of methanol added is 2, 3, 5, 10, and 10mL. The last mixture will have approximately 50 mL of ethyl acetate and 30 mL of methanol.

Be sure to turn off variac heater and water flow at completion of experiment. Clean up and leave vials to air dry. **Remove Stopcock from distillation apparatus.** If the stopcock is left in place while glass cools it will get stuck and cannot be removed.

**Analysis**

On one of the following pages is a calibration curve of index of refraction versus weight percent composition for a number of ethyl acetate - methanol solutions. Use this curve to convert your index of refraction measurements to composition for each of your measurements. Note that it will only be possible to estimate to nearest whole number such 35% ethyl acetate and not 35.2%.

Prepare a phase diagram showing the boiling point (y axis) versus the composition of the liquid and the vapor (x axis). You generate this curve by plotting one y value (temperature) against two x values (composition). In each pair, one point represents vapor and one point represents liquid. Draw a circle around each vapor point and a box around each liquid point. Include the boiling point values for pure methanol and pure ethyl acetate on your graph. Only do one temperature versus composition graph – all your data will be on this one graph. Include boiling points of both pure compounds. Draw curves through your points to generate an appropriate vapor-phase diagram. Indicate the boiling point and composition of the azeotropic mixture and compare to the literature values. Report the values of the boiling point and composition (percent of ethyl acetate) for the azeotropic mixture and compare your results to the literature values.
Stopcock positions

1. Side arm
   Boiler

2. Side arm
   Boiler
   Sample condensed vapor

3. Side arm
   Boiler
   Sample liquid
The graph shows the relationship between Wt % EtOAc and Index of Refraction. The table below lists the Wt % EtOAc and the corresponding Ref. Index for each data point:

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<th>Wt % EtOAc</th>
<th>Ref. Index</th>
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