

Boiling Point-Composition Diagram of a Binary System

Introduction

In an idealized system the boiling point of a mixture of two soluble liquids is always between the boiling points of the two pure components and the vapor pressures of each component are always equal to the vapor pressure of each pure component multiplied by the mole fraction of the component

Many binary systems differ from the idealized behavior depicted by Raoult. If two liquids form an azeotrope, for example, the boiling point may be significantly different from that of either pure substance. This makes separation of these mixtures by fractional distillation much more complex. The difficulty in predicting such mixtures makes the observation of boiling points and liquid/vapor composition important experimental work.

The purpose of this experiment is to determine such information about the cyclohexane, 2-propanol system. In week one a calibration curve of refractive index versus mole fraction will be constructed for the binary system. In week two this refractive index graph will be used to determine the concentrations of condensed vapors as well as the boiling liquids that produced them. From this information a BP - composition diagram can be constructed.

Procedure - Week One

1. Connect a tap water line to the refractometer and turn on the water. Leave it on throughout the experiment. This will provide a somewhat standard temperature for the measurement of the refractive index this week and next.
2. Fill two burets with cyclohexane and 2-propanol (isopropyl alcohol). Do not rinse with water.
3. Weigh each of 7 empty 50 ml Erlenmeyer flasks and stoppers to the nearest mg. Place approximately 1, 2, 3, 4, 5, 6, and 7 ml of cyclohexane in the flasks. Stopper and weigh to the nearest mg. Next add approximately 10.5, 9, 7.5, 6, 4.5, 3 and 1.5 ml of 2-propanol to the flasks. Stopper and weigh to the nearest mg.
4. Swirl to mix the solutions thoroughly.
5. Measure the refractive index (RI) of each pure liquid and each solution.
6. Calculate the mole fraction of cyclohexane in each flask and construct the calibration graph of RI versus MF of cyclohexane. It should be a straight line. Determine the linear regression fit.

Procedure - Week Two

Summary

This week we will collect data on the composition of the vapor and liquid for various mole fraction solutions of cyclohexane and 2-propanol. This will be accomplished by heating to the boiling point, condensing the vapor, and then measuring the refractive index of condensed vapor and liquid.

Notice on the published phase diagram that the boiling point change caused by adding 2-propanol to cyclohexane is greater than when adding a similar amount of cyclohexane to 2-propanol. It will therefore be necessary to add 2-propanol in smaller amounts to cyclohexane than when doing the reverse. With each addition the boiling point will be determined as well as the composition of both phases. The refractive index graph from last week will be used to determine the composition. If you look closely at the tip of the condenser, you will notice a lip which will hold a small amount of liquid. (One apparatus does not look like this and has a separated storage area for condensed vapor.) As the system is refluxed, the condensed vapor will run through this lip continuously and hence a sample of the vapor phase may be obtained here. Since the vapor phase will constitute only a very small percentage of the entire system, it will be quite satisfactory to cool the system to just below its boiling point and open the system and obtain a liquid sample from the pot. Because the composition is determined by direct analysis of the liquid and gas phases using the refractive index, it is not necessary to measure any volume very accurately.

Procedure

Connect a tap water line to the refractometer and turn on the water. Leave it on throughout the experiment.

Carefully remove the thermometer from the heating mantle, condenser system. If the system is not dry, blow air through it until it is dry. Add about 25 ml of 2-propanol and some boiling chips. As previously stated no great care is needed when measuring volumes. Replace the thermometer. With the heating mantle in place plug it directly into a 110 VAC outlet. Be certain a small stream of water is running through the condenser. When the temperature stabilizes, record it. Unplug and drop the the heating mantle and wait until refluxing stops. Then collect samples of the liquid phase and the condensed vapor phase and measure the refractive index of each.

Remove the thermometer long enough to add about 2 ml of cyclohexane. Insert the thermometer, reposition the mantle and plug it in. When equilibrium is reached as indicated by a constant temperature reading, read the temperature. As before obtain liquid and condensed vapor samples and measure the refractive index of each.

Return unused samples from the pipets to the reflux pot and add 4 ml more of cyclohexane. Reposition the mantle, etc. repeating for this solution and for additions of 6, 8, and 11 ml. If the boiling point rises, finish that sample but make no more additions. This completes collection of half the data necessary for a phase diagram.

Unplug and remove the mantle if it has not already been removed. Although it would be possible to continue adding cyclohexane, it is an inefficient way to obtain solutions having a high mole fraction of cyclohexane. It is far easier to start with 100% cyclohexane and add 2-propanol. Remove the solution in the pot and place in the waste container under the hood. Blow air through the system to dry it out. Add 25 ml of cyclohexane and determine its boiling point and the refractive index of its liquid and vapor phases. Now add and measure the temperature and refractive indices for solutions formed by adding 0.2, 0.4, 1.0, 4.0, 6.0 and 6.0 ml of 2-propanol (yes, 6.0 ml twice!). Be careful not to add too much during the first two additions, since a small amount of 2-propanol will cause a large change in the boiling point. As before discontinue further additions once the boiling point starts to rise.

Tips on the Results Section

Prepare a graph of boiling point of liquid versus mole fraction of cyclohexane for the liquid and vapor phases, similar to the published one. If your spreadsheet does not have a mode which allows you to smoothly "connect the dots" (sometimes called the *Interpolate* mode), then simply draw a smooth curve manually through all the points.

The final report should include:

- tables of all raw data taken
- tables of all calculated data with sample calculations
- the refractive index graph
- the phase diagram
- the experimental and literature azeotrope temperature and composition

No error analysis is needed. Other parts besides the results section may be required as well. Check with the instructor.

Reference (published diagram)

Michiels, L., Bartle, R., and de la Fuente, G., "Two Safety Improvements for a Standard Experiment on the Boiling Point-Composition Diagram of a Binary System", *J. Chem Ed.*, 59(2), 157, (1982)