EXPERIMENT 4 - BOILING POINT COMPOSITION DIAGRAMS OF BINARY SYSTEMS

THEORY:

According to Raoult’s law, ideal solutions consisting of one volatile component A, and a non-volatile component B, show the following dependence:

\[ P_T = P_A = x_A P_A^0 \]  \hspace{1cm} (1)

where \( P_T \) is the total pressure above the solution. Since A is the only volatile component, the total pressure is the same as the partial pressure of A, i.e. \( P_A \). \( x_A \) is the mole fraction of A in the solution and \( P_A^0 \) is the vapor pressure of pure liquid A at the same temperature as the solution. If the solution consists of two volatile components, A and B, then the same equation can be written as:

\[ P_T = x_A P_A^0 + x_B P_B^0 \]  \hspace{1cm} (2)

As before, \( x_B \) is the mole fraction of B in the solution and \( P_B^0 \) is the vapor pressure of pure liquid B at the same temperature as the solution. \( x_A \) and \( x_B \) represent the composition of A and B in the solution, respectively.

You can see the temperature-composition diagram of a binary mixture of A and B in Figure 1. The lower line is the liquid line below which liquid and above which vapor phases exist. Similarly the top line is the vapor line. Above this line exists the vapor phase, and below it the liquid.

![Figure 1](image)

The composition of any point in between these lines can be given by a tie-line (see the line between the two curves in Figure 1). The point on the liquid curve of this line is used to determine the composition of the liquid at equilibrium with the vapor above it. The point on the vapor curve shows the composition of the vapor phase. The composition of the vapor above the solution, however, is not the same as that in the solution. The vapor is richer in the more volatile component. This simply means the mole fraction of the more volatile component (let us say A) in the vapor, \( y_A \), is higher than \( x_A \). When distilling a binary solution, the vapor (i.e. the distillate) will be richer in e.g. A. If the distillation is repeated a few times,
eventually the vapor is expected to consist of pure A. This way, all A and B can be separated from one another. The “boiling-condensation” cycle is known as “fractional distillation”.

In the case of non-ideal solutions, it might not be possible to separate A and B completely. The systems which are impossible to separate completely are known as azeotropes (azeotrope = not changing composition when boiling). When the azeotropic composition is reached the condensate retains the composition of the boiling liquid. A maximum boiling point observed in the azeotropic mixtures (i.e. the boiling point of the azeotrope is higher than the boiling point of either component (A or B) if the interactions between A and B are stronger than those between A and A, and between B and B; A-B > A-A ~ B-B. Figure 2 is an example to high-boiling azeotropes. Similarly a minimum is observed if the vapor pressure of the binary mixture is lower than the vapor pressure of either pure A or pure B; A-B < A-A ~ B-B. Again, Figure 3 is an example to low boiling azeotropes.


![Figure 2](image1.png)

![Figure 3](image2.png)

In this experiment you will be asked to distil and separate out an azeotropic mixture and determine the azeotropic composition.

**PROCEDURE**

*It is very important that the glassware is not rinsed with H₂O!!*

- Place condensed vapor samples taken from the condenser into vials labeled with V.
- Place liquid samples taken from the distillation flask into vials labeled with L.

1. Put 90 ml of acetone into the distillation flask. Determine its boiling point by carrying out the distillation close to 56°C. Collect sample 1V from the condenser. Then cool the flask and collect sample 1L at 46°C.
2. Return the distillate from step 1 into the distillation flask. Add 10 ml of chloroform and start distillation. When the temperature reaches about 58°C, collect sample 2V from the condenser. Then cool the flask and collect sample 2L at 48°C from the distillation flask.
3. Resume the distillation procedure. Collect sample 3V at around 60°C from the condenser. Cool the flask and collect sample 3L at 50°C from the distillation flask.
4. Resume the distillation procedure and continue to about 61\(^\circ\)C. Cool the flask somewhat, and then add 17.5 ml chloroform and 32.5 ml acetone. Collect sample 4V at around 62\(^\circ\)C from the condenser. Cool the flask and collect sample 4L at 52\(^\circ\)C from the distillation flask.
5. Resume the distillation procedure and continue to about 63\(^\circ\)C. Cool the flask somewhat, and then add 25 ml chloroform and 25 ml acetone.
6. Discard the distillate.
7. Resume distillation, saving the new distillate for later use. Collect sample 5V from the condenser at around 63.5\(^\circ\)C. Cool the flask and collect sample 5L at 53.5\(^\circ\)C from the distillation flask.
8. Resume distillation, continue until the boiling point ceases to change significantly (at around 64\(^\circ\)C), then collect sample 6V at around 64\(^\circ\)C from the condenser. Cool the flask and collect sample 6L at 54\(^\circ\)C from the distillation flask.
9. Combine the residue with the distillate of steps 7 and 8, and set aside. DO NOT DISCARD! You will use it in Step 11.
10. Rinse the distillation flask with a little chloroform. Then put 40 ml chloroform into the flask, collect sample 7V at around 61\(^\circ\)C from the condenser. Cool the flask and collect sample 7L from the distillation flask at 51\(^\circ\)C.
11. Mix the distillate of step 10 with 10 ml of the “combined distillate and residue of steps 7 and 8”.
12. Resume distillation and collect sample 8V at around 62.5\(^\circ\)C from the condenser. Cool the flask and collect sample 8L from the distillation flask at 51.5\(^\circ\)C.
13. Return the distillate of step 12, and then add approximately 25 mL of the “combined distillate of steps 7 and 8”.
14. Resume distillation and collect sample 9V at around 63.5\(^\circ\)C from the condenser. Cool the flask and collect sample 9L from the distillation flask at 53.5\(^\circ\)C.
15. Resume distillation and collect sample 10V at around 64\(^\circ\)C from the condenser. Cool the flask and collect sample 10L from the distillation flask at 54\(^\circ\)C.
16. After the samples are collected, their refractive indices must be measured and recorded. This can be done at any convenient time.

**CALCULATIONS**

1. Using the refractive index values given in Table 1 for conversion, determine the mole fractions of chloroform, and hence of acetone.
2. Plot T versus x (mole fraction) using your results. Draw smooth curves a) through the points obtained for the distillate (V) and b) through the points obtained for the residue (L).
3. Label all the phases present on the graph.
4. State what kind of an azeotrope this mixture is. What is the nature of the interactions between molecules?
5. Determine the azeotropic composition and its boiling point from your graph.
6. Compare your results with those given in literature. Determine the error in your results.
TABLE 1

REFRACTIVE INDEX COMPOSITION FOR ACETONE-CHLOROFORM MIXTURES

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