Three Component Systems

Submitted by:
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Abstract:

This laboratory experiment was performed in order to produce a graph of a three component system including tie-lines. A multitude of titrations of different solutions were used in order to determine the data to produce the three-component graph (Fig. 1). The three components used for this experiment were chloroform, water, and glacial acetic acid. The three components used produce a two phase system when combined which is clearly evident in the graph of the system.

Introduction:

The basis for all component systems and their corresponding phase diagrams is the Gibbs’ phase rule. According to this rule the degrees of freedom of a system, variance, at equilibrium is equal to the number of components the system has, minus the number of phases plus 2. The equation is therefore written:

\[ v = c - p + 2 \]

Where \( v \) = is the variance
\( c \) = number of components
\( p \) = number of phases

This is also under the assumption that the equilibrium is only affected by temperature, pressure, and concentration. The variance of a system is the smallest number of independent variables one would need in order to completely fix the state of the system.

The experiment in this laboratory was carried out under conditions of equal temperature and pressure and thus the equation for variance is slightly changed:

\[ v = c - p \]

In the case with this lab a three component system is being used, which produces 2 different phases when mixed together. Therefore to calculate the value for variance:

\( c = 3 \) and \( p = 2 \)

\[ v = 3 - 2 = 1 \]

This means that if the concentration of only one component of the system is given, the concentrations of the other two components can be determined by the phase diagram of the system.

The phase diagram for a three component system is most easily represented by an equilateral triangle, where each side of the triangle corresponds to one of the components of the
system. The equilateral triangle can be divided up, each side into 100 equal parts, to produce the "triangular grid" seen in fig. 1. Therefore, one can go to any one point in the center of this grid, and know the composition of all three components at that point instantly.

The graph also shows that any point situated on one of the sides of the triangle indicates that there are two components present, with the percentages indicated. The percentages of the system must always be equal to 100, as the three components make up the complete and whole system.

The phase diagram also consists of tie lines which are lines where at which the mixture of the three components in the indicated percentages separate into two immiscible ternary solutions. That is there are only two phases present, one above and one below the tie line. The graph produced in this lab has only 2 tie lines, but each phase diagram consists of an infinite amount of tie lines. In reference to the tie line, if one were to look at the graph the following can be said for the lower tie line:

- The amount of phase M = ON/MN
- The amount of phase N = MO/MN

Also, because the tie lines in fig.1 slope upward to the right the generalization can be made that the acetic acid is more soluble in phase N, chloroform rich, then it is in phase M, which is rich in water.

All the major calculations performed on the data obtained in this laboratory are of basic nature, and require no further understanding of the procedure or concept. Therefore, all the equations needed are of a very easy degree, which will be seen later, and further explanation is not needed.

**Experimental:**

The setup for this lab is very straight forth and easy, as all one really needs are three burettes, one filled with acetic acid, one with chloroform and one with water. Furthermore, a separatory funnel will be needed, along with 0.2 N sodium hydroxide, and an assortment of glass collection bottles.

The burettes containing water and chloroform can be kept at the lab bench, while the burette containing the glacial acetic acid should be kept in the fume hood. Also, always make sure to cap anything with the glacial acetic acid contained in it, as it will easily evaporate under the conditions of the lab.

The density of each solution needs to obtained through the use of standard literature at the room temperature that the experiment will be performed under. After these numbers are obtained, solutions containing approximately 10, 25, 40 and 60 percent acetic acid in water by
weight need to be prepared. The percentages do not need to be exact, but the percentage of each must be exactly known. Each solution should be roughly 20 grams in weight, and each needs to be placed in a stoppered-glass bottle to avoid evaporating. After the solutions are at room temperature they each need to be titrated with chloroform until the first perceptible permanent cloudiness is evident. This cloudiness will be the result of the formation of a second liquid phase with a different refraction index than the original phase. During the titration, the bottle must be shaken vigorously after each addition to ensure even distribution of the chloroform.

After all four samples have been titrated; they must be stoppered and set aside. Now, samples of approximately 10, 25, 40, and 60 percent acetic acid in chloroform need to be prepared as before. This time however the solutions will be titrated using water, but to the same cloudiness end point as before.

For all eight runs the weight of each component at the first signs of cloudiness needs to be calculated, along with the weight percentage it corresponds to. These values, seen in Table 1, are what will be used to plot the phase diagram of the three-component system. The values, once plotted, should produce a noticeable arch in the triangular region.

Next, the tie lines of the curve must be determined. This is done by producing 40 mL mixtures of 10 and 20 percent acetic acid with 45 percent chloroform in each case and the rest water. The concentrations of each must be accurately known in each case.

After mixture, the solutions are allowed to reach equilibrium, and the two phases are separated by the standard use of a separatory funnel. Each phase is put in a separate glass vial, and capped. The density of each phase is then determined through the use of a picnometer and an analytical balance.

The amount of acetic acid in each is then determined by titrating it with 0.2 N sodium hydroxide solution, with the use of phenolphthalein indicator. Five milliliter aliquot of each solution is sufficient for the titration, but the exact volume used must be known accurately.

From this data the percentage of acetic acid in each solution is determined. These values, one fore the top layer and one for the bottom layer, should correspond to points on the curve, and their connection through the use of a straight line will produce a tie line on the graph. The phase diagram is now complete.

**Data:**

For each of the 8 prepared solutions in the first part of the lab, the initial amount of component present is measured used the use of a burette, along with the amount of titrate added during the titration. Once the volume of each is known in the final, titrated solution, the weight of each is determined, through the use of the known densities. From this the weight percentage of each could be determined. This data is all present in Table 1, for each of the 8 runs.
For the second part of the lab, after the titration with the sodium hydroxide is complete and the known amount of sodium hydroxide used is recorded further information is needed. The weight of the picnometer by itself, along with it containing each of the liquids separately must be determined on a precise analytical balance. With a known volume of 10 mL the picnometer then divulges the density of each solution. These results are seen in table 2, which is attached.

This information is then used in determining the concentration of acetic acid in each phase and through this the percentage of acetic acid in each phase can be determined and this can be plotted on the graph. The data from this portion can be seen in table 3.

The data as a whole from this lab, all come together in the production of figure 1, which is a phase diagram for the three component system of chloroform, water, and acetic acid, and room temperature and pressure.

**Results and Discussion:**

The data from table 1 is used to produce the general phase diagram of the system as seen in figure 1. The arc that the data produces shows us where the system changes from a one phase system to a two phase system. That is that any point above the arc indicates where the three components mix to form a one phase system, and anywhere under the curve the three components combined to form a three phase system.

The arc denoted by the system of points MPN consist the exact points at which the second phase starts to form. That is, the points at which the first cloudiness appeared in the titration are all present on the arc. A mixture of the three components in the percentages denoted by the arc will produce the same cloudy solution.

The tie lines are produced through a more extensive series of calculations but nothing very extensive. Once the density of each solution is determined through the use of the picnometer, the percentage of acetic acid needs to be determined. To do this the amount of sodium hydroxide used is converted into a molar amount. This mole amount will be equal to the amount of moles of acetic acid present in the aliquot. Therefore, the mol/mL concentration can be determined, which can be further transformed into g/mL of acetic acid.

Now, if the assumption is made that the total solution is just 1 mL the accurate percentages of the acetic acid and either chloroform or water, can be determined. To do this one just needs to take the grams of acetic acid divide it by the density of the solution determined by the picnometer, and multiply this by 100. This will give the percentage of acetic acid present, and if you subtract this from 100, the percentage of the other component will also be known. The same can be repeated for all four solutions, and two different tie lines will be produced.

The tie lines are the lines that connect the two immiscible solutions, of M and N, in equilibrium. That is along any one of the tie lines the composition of M and N are related to each
other. The amount M in a solution along the tie line is given by the ratio of ON/MN, and furthermore, the amount of N is given by the ratio MO/MN.

Although only two tie lines are present here, in a given phase diagram there are an infinite number of these tie lines. That is there are an infinite number of percentages that will produce these equilibrium states. However all tie lines, within the same graph will slope in the same direction.

In the case of figure 1, the tie lines slope in and upward direction towards the right. This tells us that the acetic acid is more soluble in the “N” phase which is rich in chloroform, than in the “M” phase rich in water. If the lines sloped upward and to the left, it would tell us the exact opposite.

The simple phase diagram produced in this laboratory can be used to determine the percentages of any of the three components of the solution by only knowing one of them. That is if you know the concentration of chloroform in the solution the other two phases can subsequently be determined from it. This is very useful, as the analysis of a solution can now take much less time, as the diagram can just be referenced for the results.

To ensure its accuracy a few more runs could be produced to make the arc curve smoother and iron out any suspect areas. Once, the results of the diagram are confirmed it could be sued throughout different experiments to save time. It could also be used as a reference in reports to determine the tendency of the three component system under different combinations at the same temperature and pressure.

If a more time was allotted, an even better curve could have produced with the use of more data points. Also, more tie liens could have been produced to see a greater trend in the tendencies of the components in the 2-phase part of the system. This said, the diagram produced is accurate with the data and substances used, and more then serves its purpose.

References:

2. “Gibbs’ Phase Rule” http://en.wikipedia.org/wiki/Phase_rule
4. “Three Component Systems” handout
### Three Component Systems

#### Phase Diagram Determination

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<th>HAc (g)</th>
<th>H2O (mL)</th>
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#### Tie Line Data

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<th>Bottom (g)</th>
<th>Density B (g/mL)</th>
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#### Tie Line Determination

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Pic. = Picnometer
Pic. Volume = 10 mL
* = 3.6 mL aliquot
Three Component Phase Diagram

Percent CHCl₃