#### PChem Experiment No. 4

#### Vapour-liquid phases for the binary system toluene-cyclohexane

#### 1. Aims

The experiment aims to create a phase diagram for a two component system of toluene and cyclohexane. This will be achieved by plotting the boiling point temperature of the system as a function of the mole fraction of toluene in the preparation.

#### 2. Introduction

A series of two component systems will be prepared, all consisting of toluene and cyclohexane. Each system will have a different ratio of toluene to cyclohexane by volume. Each mixture will be distilled in an ebulliometer. This device will allow the boiling point of each mixture to be recorded. The ebulliometer will produce a distillate and a liquid residue from each mixture.

The mole fraction of a constituent of a system is the number of moles of the constituent divided by the total number of moles in the system system. For a mixture of liquids A and B, the mole fraction of A, xA, is given by the relation:

$$x\_{A}=\frac{n\_{A}}{n\_{A}+n\_{B}}$$

Where $n\_{A} and n\_{B}$ are the number of moles of A and B in the system.

 A number of prepared solutions of cyclohexane and toluene will boil in the ebulliometer at a specific temperature, which will be recorded. At that temperature, the evaporated gas phase above the solution will be in equilibrium with the liquid phase which has not evaporated. The composition of the gas phase will be different to that of the remaining liquid (the residue). The ebulliometer distills the gas phase and collects it.

 To prepare a phase diagram for the binary system, the compositions of the distillate and residue must be determined for each solution prepared for which a boiling point has been recorded.

Gas-liquid chromatography (GLC) of samples will be carried out using a gas chromatograph.

For the toluene/cyclohexane binary system, it must be taken into account that the two compounds do not create equal detector responses. This can be corrected by multiplying the peak height of toluene by a factor of 1.04, giving the corrected peak height, $h\_{tol}^{'}$. Hence the mole fraction of toluene in the system is given by the relation $x\_{tol}=\frac{h\_{tol}^{'}}{h\_{tol}^{'}+h\_{ch}}$ , where hch is the height of the cyclohexane curve.

The mole fraction of toluene for both the vapour phase and liquid phase of a number of binary systems will be determined, each having a of different ratio of toluene to cyclohexane. Then boiling point will be plotted with respect to the mole fraction of toluene for the residues(liquid phase) and distillates(gas phase) on the same graph. This will form the phase diagram for the binary system.

#### 3. Experimental Procedure

The boiling points of pure cyclohexane and pure toluene were recorded using the ebulliometer.

A series of two component systems will be prepared, all consisting of toluene and cyclohexane. Each system had different ratios of toluene to cyclohexane by volume.

Each solution was boiled in the ebulliometer. The boiling point temperature for each solution was recorded for each prepared solution. The distillate and the remaining residue were collected in each case.

1$μ$L samples of the distillate and residue were prepared and put through the chromatograph respectively, the results of which were printed after 6 minute processing.

3 samples of pure cyclohexane also underwent chromatographic analysis and an average curve area was attained from the pure samples. This was repeated for cyclohexane.

#### 4. Results (no max.)

The boiling points for pure toluene and pure cyclohexane were attained and samples were put through the chromatograph. The results are tabulated below.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Boiling point(K) | Sample Number | Height(mV) | Area(mV s) | Average Area |
| 382.55 | Toluene Ref 1 | 342 | 3089586 | 2975002.333 |
|  | Toluene Ref 2 | 343 | 3431930 |  |
|  | Toluene Ref 3 | 266 | 2403491 |  |
|  |  |  |  |  |
| 354.15 | Cyclohexane Ref 1 | 286 | 2158180 | 2191669.333 |
|  | Cyclohexane ref 2 | 291 | 2148026 |  |
|  | Cyclohexane ref 3 | 298 | 2268802 |  |

Six binary systems were prepared and their boiling points measured. The vapour and liquid phases of each system were prepared and a sample of each underwent gas-liquid chromatography. Distinct toluene and cyclohexane peaks were observed on the resulting curve of voltage with time. The resultant peak heights and areas, for the residues and distillates of each binary system were recorded. They are tabulated below along with the boiling point temperature for the systems.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Boiling temp(K) | toluene:cyclohexane (by volume) | Toluene height (mV) | Toluene Area (mV s) | Cyclohexane height (mV) | Cyclohexane area (mV s) |
| 378.65 | 30 2 distillate | 294 | 2500905 | 119 | 477311 |
| 378.65 | 30 2 residue | 313 | 3079212 | 22.3 | 79085 |
| 374.15 | 30 5 distillate | 253 | 2112331 | 160 | 755104 |
| 374.15 | 30 5 residue | 310 | 2792889 | 56.5 | 203769 |
| 366.15 | 30 15 distillate | 172 | 1166692 | 197 | 967862 |
| 366.15 | 30 15 residue | 273 | 2779136 | 147 | 599153 |
| 362.65 | 30 25 distillate | 150 | 975058 | 242 | 1383276 |
| 362.65 | 30 25 residue | 239 | 1839586 | 191 | 884507 |
| 357.65 | 10 30 distillate | 75.9 | 448429 | 268 | 1619921 |
| 357.65 | 10 30 residue | 140 | 895876 | 245 | 1378425 |
| 360.65 | 20 30 distillate | 108 | 716781 | 249 | 1491026 |
| 360.65 | 20 30 residue | 195 | 1366301 | 214 | 1068951 |

The molar ratios of toluene to cyclohexane were calculated for each prepared solution was calculated. Values were attained using the curve area and heights respectively.

The molar ratio was calculated from the area of the respective curves as follows. The average area of the curve for a 1$μL$ sample of pure cyclohexane was calculated as in the table above. The number of moles of cyclohexane in 1$μL$ was calculated using given values for the density of cyclohexane and the molecular weight of cyclohexane:

$$n\_{ref}=\frac{\left(density\right)(0.000001)}{molecular weight}=\frac{\left(0.7885\right)(0.000001)}{84}=9.386905x10^{-9}moles$$

The number of moles of cyclohexane in each of the binary systems can be calculated using the following relation:

$$n\_{sample}=\frac{area\_{sample }}{area\_{ref}}x(9.386905x10^{-9})$$

Where $area\_{sample }$ is the area of the cyclohexane curve determined by chromatograph analysis and $area\_{ref}$ is the averaged area of the three reference samples of pure cyclohexane.

This calculation was also carried out for the toluene in sample. For these calculations, the density of toluene was taken to be 0.8669 g/mL and the molecular weight of toluene was taken to be 92.1381 g/mol. The molar ratio of toluene in the solutions was then calculated from the relation:

$$x\_{tol}=\frac{n\_{tol}}{n\_{tol}+n\_{cyc}}$$

Where $x\_{tol}$ is the molar ratio of toluene and $n\_{tol}$ and $n\_{cyc}$ are the respective number of moles previously calculated for the vapour and liquid phases of each system.

Then the boiling point temperature was plotted as a function of the molar ratio of toluene in the vapour and liquid phases respectively.

The molar ratios of toluene to cyclohexane can also be calculated using the height of their resultant curves. The boiling point was subsequently plotted as a function of the molar ratio of toluene attained using the adjusted peak height for toluene, $h\_{tol}^{'}$, in the relation $x\_{tol}=\frac{h\_{tol}^{'}}{h\_{tol}^{'}+h\_{ch}}$ as follows:

#### 5. Discussion and Conclusions

The phase diagram was obtained for the toluene-cyclohexane binary system using molar ratio values obtained from the area enclosed in respective voltage curves and the heights of peaks, respectively. The measurement of 1$μL$ for use in the chromatograph had a margin of error of 0.1$ μL$. The measurement of the boiling point temperature was also subject to inaccuracy. These potentially contributed to inaccuracy in the phase diagram.

#### Answer the following post-practical questions

1. From your phase-diagram, does the toluene-cyclohexane system form an azeotropic mixture?

The phase diagram does not display an azeotropic point.

1. If the distillate from a 50:50 toluene-cyclohexane mixture is re-distilled, use your phase diagram to estimate the composition of the second distillate.

Using the phase diagram derived from the areas of voltage curves, the re-distillate would have a composition of roughly 25:75 toluene-cyclohexane.

1. What is a eutectic mixture?

A eutectic mixture is a mixture for a specific mix of compounds or elements which has the lowest melting point of all ratios of the components. In a liquid-solid two-phase diagram, the eutectic point occurs at the eutectic temperature and the eutectic mixture.

1. Apply the phase rule to the three regions of your phase diagram and interpret the number of degrees of freedom in each case.

The Gibbs’ phase rule is as follows:

$F=C-P+2$, where F is the number of degrees of freedom, C is the number of components of the system and P is the number of phases in equilibrium at the area under scrutiny. For the vapour only and liquid only regions of the diagram the number of degrees of freedom is 3. For the vapour and liquid region, there are 4 degrees of freedom.

#### PChem Experiment 4

#### Pre-practical questions:

1) What is an azeotrope?

This is a point at which liquid and vapour curves intersect in a binary system phase diagram. At that specific molar ratio and boiling temperature, the vapour phase in the binary system is of the same molar ratio as the liquid phase. The molar ratios of constituents cannot be changed by distillation because of this.

2) What is the significance of a triple point on a one component phase diagram?

In a one component phase diagram the triple point is the specific temperature and pressure at which three phases (vapour, liquid, solid) coexist in thermodynamic equilibrium.

3) Discuss briefly how a gas-liquid chromatograph works.

. In GLC analysis, the analyte is vaporized and suspended in an unreactive or inert carrier gas. This mobile gas phased is moved through a long tube (the column).The walls of the column are coated with the liquid stationary phase. Different compounds will elute at different time intervals though the stationary phase, known as the retention time of the compound. The gaseous analyte then passes through a thermal conductivity detector (TCD). A simplified circuit diagram of the detector is included.



 The carrier gas is used as reference in this detector as all compounds will have a different thermal conductivity.

The column flow containing the eluent and the reference are passed across respective thermistors in the Wheatstone bridge arrangement illustrated the diagram. The analyte will have a greater thermal conductivity than that of helium and hence the thermistor will gain heat energy and increase in resistance. This will cause a potential difference and flow of current across the voltmeter at the centre of the Wheatstone bridge. This increase in voltage will occur at the characteristic retention time of the analyte. Also, for a multiple constituent system, such as the binary system under scrutiny, the compounds will create a voltage at different times depending on the respective retention time of constituents. The magnitude of respective voltages will also correlate to the molar fractions of constituents of the binary system. These magnitudes will be displayed as a plot, with voltage (in millivolts) on the y-axis and time on the x-axis. For a given constituent x, the voltage created will form a peaked curve, of height (hx) which will occurrence with time will be characteristic of its retention time.

Name \_\_\_\_\_\_\_\_\_\_\_\_\_Louis Gregg\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Student Number\_\_\_\_\_\_\_10336691\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Date \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_08/04/2012\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Lab Partner’s Name: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_Richard Durning\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Demonstrator \_\_\_\_\_\_\_\_\_\_\_?\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_