#### PChem Experiment No. 3

#### Cryoscopic determination of molecular weight

#### 1. Aims

The experiment aims to calculate the molecular weight (M) of benzoic acid. Several amounts of benzoic acid of known mass are to be placed in cyclohexane solvent. This is to be carried out by observing the change in a colligative property of the solution, the freezing point depression, with the amount of benzoic acid added.

Also, by comparing our result with the standard value, Raoult’s law for the relationship of the vapour pressure of a solution to the mole fraction of solvent added can be verified.

#### 2. Introduction

In a binary system such as the presence of a solute in a solvent, the vapour pressure of the solvent is lowered. This results in the temperature at which the solvent and solute come into equilibrium being lowered (freezing point depression).The magnitude of this depression is related to the molarity and the molecular weight (M) of the solute, rather than it’s chemistry or reactivity.

Raoult’s law states that the contribution, ,to vapour pressure above an ideal solution from any component, J is given by , where is the mole fraction of J and is the vapour pressure of pure J.

For dilute solutions, where the mole fraction for everything but the solvent (in this experiment, cyclohexane)is small, their contributions to the vapour pressure can be ignored. For a binary system (solvent S, solute J) the mole fractions are related according to . The Raoult’s law for the solvent becomes .

Colligative properties all stem from the reduction of the chemical potential of the solvent dues to the presence of a solvent. Letting be the chemical potential of the pure solvent the chemical potential of the solution is given by . Equilibrium for the solution is established at the temperature for which

Then rearranging the equation to give :

Differentiating both sides with respect to temperature and using the Gibbs-Helmholtz equation (, the equation above becomes

By multiplying both sides by dT, integrating the left hand side from 0 to ln, the right hand side from the freezing point of pure cyclohexane( to the boiling point of the solution(T) and then equating ln to ln the equation becomes:

Taking into account that and because the equation becomes:

Hence by substituting in the appropriate physical constants for cyclohexane, the change in boiling point depression is given by

Where n is the number of moles of solute and W is the mass of cyclohexane.

This can be extended to include the molecular weight of the solute, which we are trying to obtain in the form:

Where w is the mass of the solute present and M, is it’s molecular weight.

#### 3. Experimental Procedure

The mass of an amount of pre-cooled cyclohexane was recorded and found to be 19.5g. The cyclohexane was poured into a freezing point tube. A dry thermometer and stirrer were inserted into the tube through its cork, such that they were immersed in cyclohexane. A 2L flask was filled with water and ice and the FP tube was then inserted into the water. Stirring the cyclohexane continuously, the change in temperature of the cyclohexane was recorded with time until the temperature became constant. This process of cooling with time was repeated twice, each time until the temperature became constant. The average temperature at which the cyclohexane stopped cooling was found and taken to be the freezing point of pure cyclohexane. An amount of Benzoic acid of mass 0.12g was added to the cyclohexane. The process of recording temperature at set increments of time as the solution cooled in the ice bath was again repeated 3 times to find an average freezing point. Subsequently, two more masses of benzoic acid were added ( 0.11g and 0.12g) and for each addition the process of recording temperature change with time during cooling was repeated 3 times.

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

The freezing point of pure cyclohexane was recorded three times across the three cooling curves and the average value was found to be 279.733C+/- 0.144338. The freezing point of the solution containing 0.11g benzoic acid was averaged and found to be 279.19+/- 0.07C.The freezing point of the solution containing 0.23g benzoic acid was calculated to be 279.256 +/- 0.011C. The freezing point of the solution containing 0.34g benzoic acid was calculated to be 279.017 +/- 0.115C. is plotted as a function of mass of benzoic acid in the solution below:

Applying the equation

to the curve, the value for the slope, 2286.2 can be equated to and taking the value of W to be 0.0195kg, the molecular weight of benzoic acid was calculated to be 2.1433kg/mol.

#### 5. Discussion and Conclusions

The relationship of averaged depression of freezing point of the solution with mass of substrate added was successfully graphed. However the values obtained for freezing point depression did not trend linearly with good accuracy. The value of the plot was 0.6764. Using the slope of the plot the molecular weight of Benzoic acid was calculated to be 2.1433kg/mol.

#### Answer the following post-practical questions

The molar mass of benzoic acid as calculated by the periodic table is 122g/mol. The value obtained in our experiment has a percentage error of 1656.8%. As the depression in melting point is colligative, it depends on the molar ratio of solute in the solution. This factor could have been affected by the rusting of the stirrer in the solution adding to the combined molar ratio of solutes.

In cyclohenxane:

In water:

The cyclohexane has a of 4.204 and hence dissociates readily in water. This would affect the amount of solute (‑) in the solvent, water. This would make the colligative effects fare more complex.

#### PChem Experiment 3

#### Pre-practical questions:

1) Verify that the freezing point depression for cyclohexane follows:

For an ideal solution the freezing point depression is given by where is the crypscopic constant, which is dependent on the properties of the solvent, not the solute and m is the molarity(number of moles n, per mass solution) of solute in the solution. Taking for the solution to be 20.8, the equation becomes:

2) Why do binary solutions freeze over a range of temperatures rather than at one precise melting point?

The presence of a solute in a solution increases the overall chaotic nature of the motion of particles in the solution because the non-uniform arrangement of molecules in the solution hampers crystallisation. This is true of all ratios in a binary system, except for the eutectic composition, which melts at only one temperature. That is the point at which the liquid and crystal phases of all species in the solution exist in equilibrium.

3) Explain why the vapour pressure of a solvent is lowered by a non-volatile solute.

If the solvent molecules are volatile then they can escape from the surface of the solution and lower the vapour pressure. If non-volatile molecules are a solute in the solution then they occupy spaces on the surface of the solution which could be from which volatile solvent molecules could escape from the surface, and in doing so, prevent the lowering of the vapour pressure.

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

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

Date \_\_\_\_\_\_\_20/10/2011\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

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