UNIT 8 DEPRESSION OF FREEZING POINT

Structure

8.1 INTRODUCTION

In this unit, you will study how to determine the molar mass of a non-volatile solute by Rast Method. This method is based upon the measurement of depression of freezing point of a solvent by addition of a known amount of non-volatile solute. The depression of freezing point is a colligative property, since it depends on the number of non-volatile solute particles in solution. The only condition is that the solute should not associate or dissociate in solution. Osmotic pressure, relative lowering of vapour pressure and elevation of boiling point are some other examples of colligative properties, which you might have studied in detail in Unit 12 of the CHE-04 course.

After studying this unit and having performed the experiment described in the unit, you should be able to:

- explain what is meant by colligative property,
- give examples of colligative properties,
- state the relation between depression of freezing point and molality of the solution,
- define molal depression constant, and
- determine molar mass of a solute by measuring depression of freezing point.

8.2 EXPERIMENT 7 : DETERMINATION OF MOLAR MASS BY RAST METHOD

This method was devised by Rast in 1922. Rast method is actually a micro-method because only a few milligrams of the solute are required. This method can be used for determining the molar mass of those non-volatile solutes which dissolve in molten camphor and do not react with it or decompose at its melting point. The molal depression constant of camphor is very high, i.e., 40.00 K kg mol^{-1}. It means that when one mole of a solute is dissolved in one kilogram of camphor, the depression in freezing point is 40°C, which can be read using an ordinary thermometer. Thus, there is no need of using a costly Beckmann thermometer to measure the depression in freezing point. In this method, we actually measure the depression in melting point of camphor. But, the melting point of solid phase and the freezing point of liquid phase of any substance are the same. Therefore, it does not make any difference whether we measure depression in the melting point or depression in the freezing point.

8.2.1 Principle

When a non-volatile solute is added to a solvent, it lowers the freezing point of the solvent. The relationship between the molar mass of a non-volatile solute and the depression in freezing point of a solvent has been discussed in Unit 12 of the CHE-04 course. We shall use Eq. 12.37 from this Unit for this purpose of determining molar mass of a non-volatile solute by Rast method.

$$\Delta T_f = \frac{K_f w_2}{w_1 M_2} \qquad \text{... (12.37)}$$

where $K_f = \dfrac{RT^2 M_1}{\Delta H_{fus}}$ = molal depression constant

Eq. 12.37 can also be written as

$$M_2 = \frac{K_f w_2}{\Delta T_f w_1} \qquad \text{... (8.1)}$$

where w_1 and w_2 refer to the masses of the solute and solvent (camphor), respectively, M_2 stands for the molar mass of the solute and ΔT_f refers to the depression in melting point of the solvent.

ΔT_f = Depression in Melting point of the solvent
= (Melting point of the solvent) – (Melting point of the mixture)
= $T_0 - T_1$

In Eq. 8.1, w_1 and w_2 are in kg unit, M_2 is in kg mol^{-1} units and K_f is in K kg mol^{-1} units. The molal depression constant of camphor is 40.0 K kg mol^{-1}. w_1, w_2 and ΔT_f are experimental quantities. Thus, using Eq. 8.1, you can calculate the molar mass of the given solute.

If you want to study more about the depression of freezing point and other colligative properties, go through Unit 12 of the CHE- 04 (physical chemistry) course.

SAQ 1

The molal depression constants of water, acetic acid, cyclohexane and camphor are 1.85, 3.90, 20.20 and 40.00 K kg mol^{-1}, respectively. Which of the above four you would prefer for determining the molar mass of a non-volatile solute and why?

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8.2.2 Requirements

Apparatus

1. Beaker 100 cm^3 — 1
2. Capillary tubes — 5
3. One-tenth degree thermometer — 1
4. Thiele's melting point tube — 1
5. Test tube — 1

Chemicals

1. Camphor
2. Acetanilide, urea or thiourea
3. Liquid paraffin

8.2.3 Procedure

Prepare a homogeneous mixture of the solute and camphor. For this, take a clean and dry test tube and weigh it accurately on an analytical balance. Put about 200 mg of the solute in it and weigh it. Now add approximately 3 g of camphor to the test tube and note down its mass. Seal the open end of the tube on the flame by drawing a capillary. Melt the mixture by placing it in a beaker containing liquid paraffin. Continue heating till the mixture melts completely and the temperature of the bath is about 5° above the melting point of pure camphor i.e., 177°C. Mix the contents of the tube by rotating it. Now cool the tube quickly in a water bath. Repeat the process of heating and cooling the mixture two more times to ensure homogeneity. Cut off the sealed end of the tube, take out the solid and powder it with pestle and mortar. Fill it in a capillary tube after sealing its lower end. Stick it to a thermometer after wetting it with the bath liquid and set up the apparatus for determining melting point as shown in Fig. 1.9 of Unit 1 of this course.

Heat gently and determine the melting point of the mixture as described in Section 1.9. Watch the melting of crystals in the capillary and note the temperature on the thermometer when the last crystals have just melted. This gives the melting point of the mixture. Allow the bath liquid to cool so that the liquid in capillary freezes. Find the melting point of the mixture again. In this way, take three readings to confirm the results and calculate the average value.

Fill another capillary with pure camphor powder and in the same manner determine its melting point. Take three readings in this case also and determine the average value.

8.2.4 Observations

Record your observations as under:

i) Mass of the empty test tube = ... g

ii) Mass of the test tube + solute = ... g

iii) Mass of the test tube + solute + camphor = ... g

iv) Melting point of the mixture

a) .... b) .... c) ....

v) Melting point of pure camphor

a) .... b) .... c) ....

8.2.5 Calculations

Mass of the solute taken = w_2 = ii) – i) = ... g = ... kg

Mass of camphor taken = w_1 = iii) – ii) = ... g = ... kg

Average melting point of mixture = T_1 = ... °C = ... K

Average melting point of camphor = T_0 = ... °C = ... K

Depression in melting (freezing) point = $\Delta T_f = T_0 - T_1$

Molal depression constant of camphor = K_f = 40.00 K kg mol^{-1}

As w_1, w_2, K_f and ΔT_f are known, calculate the molar mass of the solute using Eq. 8.1.

$$M_2 = \frac{K_f\, w_2}{\Delta T_f\, w_1}$$

8.2.6 Result

The molar mass of the solute as determined by Rast method = ... $kg\ mol^{-1}$

Calculated molar mass of the solute = ... $kg\ mol^{-1}$

8.3 SUMMARY

In this unit you studied the determination of molar mass of a non-volatile solute by Rast method. This method is based upon the measurement of depression in freezing point of a solvent by addition of a known amount of the solute. Depression of freezing point is a colligative property as are elevation of boiling point, osmotic pressure and lowering of vapour pressure. Colligative properties depend on the number of solute particles present in solution, but not on their nature.

8.4 TERMINAL QUESTIONS

1. What is a colligative property?
2. For what type of solid compounds Rast method can be used?
3. What is molal depression constant?

8.5 ANSWERS

Self Assessment Question

1. The value of molal depression constant of camphor is the largest of the four solvents. Therefore, a given amount of solute will produce the largest depression in freezing point, if camphor is taken as a solvent. Thus, camphor would be the obvious choice provided that the solute dissolves in molten camphor and does not react with it or decompose at the melting point of camphor.

Terminal Questions

1. The property which depends only on the number of solute particles and not on their nature is called a colligative property.

2. Rast method can be used only for those compounds which dissolve in molten camphor, do not react with it and do not decompose at its melting temperature.

3. Depression in freezing point of the solvent when one mole of the solute is dissolved in one kg of the solvent is known as the molal depression constant.