MOLECULAR WEIGHT BY FREEZING POINT DEPRESSION

BACKGROUND

This experiment demonstrates the use of colligative properties. The goal is to measure the molecular weight of a non-volatile solute by determining the concentration dependence of the freezing point depression of a solution. The solvent used must be one of the compounds commonly referred to as volatile; that is, it must have an appreciable vapor pressure. One of the several useful aspects of colligative properties is the fact that the vapor pressure of volatile solvents is lowered when a non-volatile solute is used to make a solution. The result is that such a solution will necessarily have a lower freezing point than that of the pure solvent. The lower freezing point is due to the fact that the vapor pressure curve for the liquid solution intersects the vapor pressure curve for the solid at a lower temperature. It must be remembered that the freezing point depression being investigated in this experiment is a property of the solution as a whole and, for ideal dilute solutions, is directly proportional to the solute concentration as shown in Equation 1.

\[ \Delta T_f = m \cdot K_f \]  \hspace{1cm} (1)

In Equation 1, \( m \) is the solution molality and \( K_f \) is the freezing point depression constant which is a function of the solvent not the solute. The value of \( \Delta T_f \) is the freezing point of the pure solvent, \( T_f^* \), minus that of the solution. Based on the definition of molality it is possible to rearrange Equation 1 into Equation 2 in order to isolate the solute molecular weight, \( M \).

\[ M = \frac{[g \cdot K_f]}{[G \cdot \Delta T_f]} \]  \hspace{1cm} (2)

In Equation 2, \( \Delta T_f \) is the freezing point depression of a solution containing \( g \) grams of solute in \( G \) kilograms of solvent. Equations 1 and 2 assume non-volatile and non-electrolyte solutes in ideal dilute solutions. Since colligative properties are independent of the identity of the solute, depending only on total particle concentration, it is possible to obtain important information about electrolytes by measuring freezing point depressions. This is especially true in the case of weak electrolytes that are only partially dissociated in solution. To the extent that a solute dissociates in solution the net number of actual particles present will increase. A larger number of particles in solution will result in a larger measured freezing point depression, \( \Delta T_f \), because the molality, \( m \), in Equation 1 will be larger. In the case of a weak electrolyte it is more appropriate to re-write Equation 1 as shown in Equation 3.

\[ \Delta T_f = K_f \cdot m_{app} = K_f \cdot \left[ \frac{g}{(G \cdot M_{app})} \right] \]  \hspace{1cm} (3)

In Equation 3 \( m_{app} \) is the “apparent” total particle molality that results from the partial dissociation of the solute. \( M_{app} \) is a weighted average molecular weight representative of the actual ions and molecules as they exist in solution. The value of \( m_{app} \) may be evaluated in terms of the analytical molality, which is based on formula weight of solute, and the percent of the solute particles which undergo dissociation, \( \alpha \), as shown in Equation 4.
In Equation 4, \( n \) represents the number of ions produced by the dissociation of one molecule of solute while \( m_o \) represents the molality based on the formula weight of the solute ignoring any dissociation. Equation 4 can be rearranged into equation 5 where \( g \) and \( G \) have the same meaning they did in Equation 2 while \( M_o \) is the actual formula weight of the solute.

\[
m_{\text{app}} = n \cdot \alpha \cdot m_o + (1 - \alpha) \cdot m_o
\]

\( \text{Equation 4} \)

The value of \( m_{\text{app}} \) may be evaluated as shown in Equation 6 with \( g \), \( G \), and \( M_{\text{app}} \) as previously defined.

\[
m_{\text{app}} = \frac{g}{G \cdot M_{\text{app}}}
\]

\( \text{Equation 5} \)

Equations 5 and 6 may be combined to show that

\[
\alpha = \frac{[M_o - M_{\text{app}}]}{[M_{\text{app}} \cdot \{n - 1\}]}
\]

\( \text{Equation 6} \)

Since \( M_{\text{app}} \) may be evaluated from the freezing point depression as shown in Equation 3 it is easy to determine the degree of dissociation of a weak electrolyte using Equation 7.

**Inter-particle Forces**

In addition to the influence of electrolyte behavior the freezing point of solutions may be affected by the way in which solute particles interact with one another. Typically attractive forces exist between solute particles. These forces can have an influence on the value of the molecular weight as calculated using Equation 2. Equation 2 suggests a possible approach to attempt to correct for such inter-particle forces. A plot can be constructed of calculated molecular weight on the y-axis versus solution molality on the x-axis. Such a plot is extrapolated to zero molality, the y-intercept, to obtain what is referred to as the limiting molecular weight. This infinite dilution extrapolated molecular weight value may be thought of as the value of the molecular weight that would be obtained if only a single molecule were present in solution. Such a technique has the result of minimizing the influence of inter-particle forces.

Since Equation 2 requires values for the \( K_f \) constants the values for common solvents are shown in Table 1.

A final note of caution is appropriate. The heart of this experiment is the measurement of how the freezing point of a pure solvent **changes** as a solution is prepared. The only reliable manner to accomplish this measure of temperature change is to make an actual measurement of the freezing point of the pure solvent at the actual laboratory conditions rather than depending on literature values. Failure to actually measure the freezing point of the pure solvent under the laboratory conditions using the same equipment that the solution freezing points are measured
can give rise to serious errors! It is also good to use one thermometer throughout in order to avoid any potential problems associated with faulty thermometer calibrations.

### TABLE 1: freezing point depression constants

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Freezing Point, $T_f^*$ (deg C at 760 torr)</th>
<th>$K_f$ (molal / deg @ 1 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camphor</td>
<td>178.4</td>
<td>37.7</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6.5</td>
<td>20.0</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>25.1</td>
<td>37.7</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>80.2</td>
<td>6.9</td>
</tr>
<tr>
<td>Water</td>
<td>0.0</td>
<td>1.855</td>
</tr>
</tbody>
</table>

### PROCEDURE

**Apparatus and Materials Needed**

1. Dewar flask of one-liter capacity fitted with 2-hole cork stopper and stirrer.
2. Digital thermometer capable of measuring to 0.1°C (Beckmann thermometer is better if available).
3. Solvent(s) listed in Table 1 as directed by instructor.
4. Hydrochloric acid solution; approximately 0.25 M.
5. Sodium hydroxide solution; approximately 0.1 M (standardized).
6. A 0.25 M solution of acetic acid or monochloroacetic acid.
7. Ten milliliter pipette

**Freezing Point Measurement:**

Place enough distilled water in the dewar flask to fill it about one-fourth full. The distilled water should be thoroughly chilled in an ice bath before being placed in the dewar flask. Add a roughly equal volume of clean crushed ice that has been prepared by freezing distilled water. It is important that the ice not contain any dissolved impurities, especially electrolytes. If the ice is not free of contaminants the freezing point of the ice bath will decrease progressively as more and more ice melts producing an increasingly concentrated solution. It may prove helpful to rinse the ice with chilled distilled water before it is placed in the dewar flask.

Position the cork stopper and insert the thermometer and stirrer into the ice water mixture. Stir the mixture until a stable temperature is indicated and record this temperature. Carefully drain off and discard the water and replace it with a like amount of the 0.25 M hydrochloric acid solution. Stir this mixture until a stable temperature is indicated on the thermometer and record this temperature. Using a 10-ml pipette withdraw two aliquots of the HCl/water mixture and place it in separate 125-ml Erlenmeyer flasks which have been previously weighed on an analytical balance. This is necessary since the concentration in this experiment must be dealt
with in terms of molality. Titrate these aliquots with the sodium hydroxide solution. Based on the titration data the amount of hydrochloric acid may be determined and by difference the amount of water solvent so that the solution’s molality may be evaluated.

The hydrochloric acid remaining in the dewar flask is diluted with sufficient chilled distilled water to result in a solution that is approximately one-half its original concentration value. The freezing point of this diluted solution is measured as before. As before, two aliquots are removed and titrated with the sodium hydroxide. The process of dilution to one-half the concentration, freezing point measurement, and titration is repeated twice more so that a total of four different solutions have been measured.

The dewar flask is emptied and thoroughly rinsed. Add enough of the chilled 0.25 M weak acid solution (acetic or monochloroacetic acid) to fill the flask about one-fourth full. Add an equal volume of clean ice and proceed as before to measure the freezing point and titrate aliquots. Just as with the hydrochloric acid the weak acid solution is successively diluted and its freezing point measured followed by titration with the sodium hydroxide. A total of four separate weak acid solutions are thus measured.

CALCULATIONS

Equation 2 may be used to calculate the molecular weight of the solute for each of the different solution concentrations. Use \( g \) and \( G \) for each of the solutions to calculate the molality of the solution. Prepare a graph of molecular weight, \( M \), on the y-axis versus the solution molality, \( m \), on the x-axis. The resultant line may be extrapolated to zero molality to obtain what is referred to as the “limiting molecular weight, \( M_{\text{infinite}} \)”. Calculate the degree of dissociation of the solute for each of the solutions whose freezing points have been measured. Prepare a plot of the degree of dissociation, \( \alpha \), on the y-axis versus the molality, \( m_0 \), on the x-axis and extrapolate to zero concentration to obtain a limit at infinite dilution of the degree of dissociation, \( \alpha_{\text{infinite}} \).