

# Vapor Pressure Osmometer

## **Introduction**

Determination of the molar mass of polymers is of considerable importance because the chain length is a controlling factor in the evolution of solubility, elasticity, fiber formation, and mechanical strength properties. Methods used to determine the molar mass are either relative or absolute. Relative methods require calibration with samples of known molecular weight and absolute methods require no such calibration. This report will focus on the use of membrane and vapor pressure osmometry to determine the number average molecular weight ( $M_n$ ). These techniques are useful in different  $M_n$  ranges and depend on the change in osmotic pressure and the lowering of vapor pressure (respectively) by polymers in solution.

## **Membrane Osmometry**

### **Introduction and Theory**

Membrane osmometry is an absolute technique which determines  $M_n$ . The solvent is separated from the polymer solution by a semipermeable membrane which is tightly held between the two chambers. One chamber is sealed by a valve with a transducer attached to a thin stainless steel diaphragm which permits the measurement of pressure in the chamber continuously. The solvent chamber is filled with solvent and closed to the atmosphere except for the solvent passage through the membrane while the solute chamber is left open to the atmosphere. The solute cannot flow in this case but the solvent can flow through the membrane. The chemical potential of the solvent is much higher than that of the solute, therefore there is a tendency for flow to occur from the solvent through the membrane to the polymer solution. Because the solvent is permitted through the membrane a change in concentration causes the solvent to diffuse to the solute side of the chamber. As this occurs, the pressure of the solvent decreases until the pressure difference across the membrane just counteracts the chemical

potential difference caused by the solute. This pressure reduction required to equilibrate the chemical potential on both sides of the membrane is regarded as the osmotic pressure. It is the pressure required in order to affect the activity of the solvent and solution equal to that of the solution. The osmotic pressure is related to the change in chemical potential by the following equation:

$$(\mu_1 - \mu_1^0) = -V_1\pi$$

where  $\mu_1^0$  = chemical potential of pure solvent  
 $\mu_1$  = chemical potential of solvent in solution  
 $V_1$  = molar volume of solvent in solution  
 $\pi$  = osmotic pressure

Examining the osmotic pressure in terms of the free energy of mixing phenomena, the change in chemical potential can be related to the polymer molecular weight by substitution of the above equation into the following:

$$(\mu_1 - \mu_1^0) = -RT \left[ \frac{c_2 V_1}{M_2} + v_2^2 (1/2 - \chi_1) c_2^2 \right]$$

where  $M_2$  = polymer molecular weight  
 $v_2$  = partial specific volume of polymer  
 $\chi$  = interaction parameter  
 $c_2$  = solute concentration

The relationship of molecular weight to osmotic pressure is then simplified to:

$$\pi/c_2 = RT/M_2 + RTv_2^2/V_1(1/2 - \chi_1)c_2$$

The first term of this equation is the van't Hoff expression for osmotic pressure at infinite dilution. The second term is the deviation from ideal behavior of the polymer solution and is related to the second virial coefficient. The relationship between the second virial coefficient and the interaction parameter is illustrated by:

$$A = RTv_2^2/V_1(1/2 - \chi_1)$$

When the interaction parameter is equal to 1/2 and the second virial coefficient is zero, then the osmotic pressure is governed by the ideal solution law.

Experimentally, in calculating the molecular weight, osmotic pressure must be measured at several different concentrations.  $\pi/c_2$  is determined for each concentration and plotted  $\pi/c_2$  versus  $c_2$ , extrapolating the concentration to zero. The slope of the resultant line is the second virial coefficient and the molecular weight is calculated by the intercept.

### **Procedure for Use of Membrane Osmometer**

The instrument on the polymer floor contains two main components, the cell assembly and the electronics-recorder assembly. Membrane conditioning is extremely important in using this technique. Membranes are usually cellulose derivatives and shipped in alcohol or aqueous solution. For aqueous solutions, simply rinse the membrane off with distilled water and place in the osmometer. The distilled water needs to be rinsed through the instrument several times while stabilizing the cell temperature. When an organic solvent needs to be used in place of water, several steps need to be taken in order to gradually introduce the membrane to this solvent. Every two hours, the concentration of a solution containing water and isopropanol is increased until a 100% concentration of isopropanol is used. Then isopropanol and the chosen organic solvent are used in the same manner described above until a 100% concentration of the organic solvent is used. Conditioning membranes in organic solvents causes the membranes to shrink therefore the membrane must have a larger diameter initially in order to compensate for this shrinkage. The required diameter for our instrument is 50mm.

The next step is to set the temperature controls to coarse 2 and fine 200 and turn on the instrument's power. Turn the pressure range gauge to 10 and set the recorder range to 1mV. The membrane is installed by first removing the top half of the cell cover and adding solvent to the cell assembly via syringe. Place the membrane (the membrane always needs to be wet with solvent so the membrane will not dry out) between the two aluminum plates and trim the membrane to the correct size to fit the center of the circular ring. Cover the membrane with solvent and tighten the membrane onto the circular ring. Fill the glass level tube with solvent and open all valves, pushing the solvent through three times. Close the solution drain valve and flush with solvent three times and then close the solvent drain valve and flush the solvent chamber three times. Close the solution drain valve and lower the level in the inlet tube with the solution drain valve to the top of the Swagelok fitting. Replace the cell cover and allow the instrument's cell temperature to stabilize. It is very important to remove air from both sides of the membrane in order to obtain accurate results. Open the solution drain valve in order to reduce the level to a reference level of sixty percent. Close the solvent inlet valve slowly and reduce that level to sixty percent.

The instrument is now ready to be calibrated. Connect the glass calibration tube to the inlet tube and then fill with solvent. Reduce the level in the calibration tube to the top mark and adjust the recorder to zero. Then reduce the solvent level 5 cm to the second mark on the tube. Adjust the calibrate control on the front of the panel to provide a half-scale reading. Then further reduce the solvent 10 cm from the top mark and calibrate as stated above. Remove the calibration tube and reset to the sixty percent reference point. It is important to note that if water is not the solvent used, then the specific gravity of the solvent needs to be multiplied by the chart recorder reading during calibration in order to obtain accurate results.

It is a good idea to run a test sample before making measurements on the polymer sample. To obtain the molecular weight of the polymer sample, the general requirement is to take measurements at three to four different concentrations. These solution concentrations should be in the range of 10g per liter to 1.8g per liter. Close the solvent inlet valve and set the solvent level to a reading of 60 and allow the cell and the recorder to stabilize. Then add 0.5 to 1.0 ml of the polymer solution and open the solution drain valve until that level meter also reads 60. Do not allow the sample level to fall below the reference level. Allow for stabilization and read the osmotic pressure off of the recorder in cm of solvent pressure. Do this for each solution in order of increasing concentration and record all osmotic pressure results. Divide each pressure by the corresponding concentration and plot these values versus concentration. The intercept is then used to calculate the molecular weight.

### **Advantages and Disadvantages**

The problems of this technique are caused mainly by the membrane. There are problems with membrane leakage and asymmetry. Membrane asymmetry is observed when both cells are filled with the same solvent but have a pressure difference between the two cells caused by membrane leakage, compression, solute contamination, or temperature gradients. Ballooning is another problem which is caused by pressure differentials and is detected by measuring the pressure change as the solvent is added or removed from the solvent cell. This effect is due to the viscoelastic nature of the membrane used. Rapid membrane degradation can also be a problem if harsh solvents are used or if the membrane is not kept moistened. Careful

preparation of the membrane is also needed in order to ensure no holes are present. The presence of dissolved air is also a problem, so all solvents and solutions must be degassed before insertion into the cells. Overestimation of molecular weight can occur if low molecular weight molecules penetrate the membrane. This causes a decrease in  $\pi$  by not being on the sample side and compensates by changing the chemical potential on the solvent side. Therefore, polymers of high polydispersity are not well suited for membrane osmometry. Polyelectrolytes can cause a problem due to the fact that  $\pi/C$  values may be higher for these solutions in the absence of added salt and may increase with dilution.

The main advantage of membrane osmometry is that it yields an absolute  $M_n$  for a polymer and calibration with standards is not required. Low molecular weights can be tolerated because they readily equilibrate on both sides of the membrane. Results are easily obtained for graft or copolymers because membrane osmometry is independent of chemical heterogeneity. This method is applicable to polymers having a broad range of molecular weights with the low end being governed by membrane permeability and the upper limit determined by the smallest osmotic pressure that can be measured. The most common range for determining molecular weights by this method is 5,000 to 500,000 (5000 for the state of the art instruments). The most common membranes typically can determine  $M_n$  as low as 10000-20000. Membrane osmometry also provides information about polymer-solvent interactions derived from the second virial coefficient.

## Vapor Pressure Osmometry

### Introduction

The determination of  $M_n$  by the use of vapor pressure osmometry operates on the principle that the vapor pressure of a solution is lower than that of the pure solvent at the same temperature and pressure. At sufficiently low concentrations, the magnitude of the vapor pressure decrease is directly proportional to the molar concentration of solute. Monitoring vapor pressure versus a change in concentration of solute can be used in a manner similar to that of membrane osmometry.

The derivation to relate  $M_n$  to vapor pressure is founded in the basic equations of dilute solution chemistry and physical chemistry. In a dilute solution, the vapor pressure of a solvent is given by Raoult's Law:

$$P_1 = P_1^0 x_1 \quad \text{where} \quad \begin{array}{l} P_1 = \text{partial pressure of solvent in solution} \\ P_1^0 = \text{vapor pressure of pure solvent} \\ x_1 = \text{mole fraction of solvent} \end{array}$$

By definition,  $x_1 = 1 - x_2$  where  $x_2$  is the mole fraction of solute so  $P_1 = P_1^0 (1 - x_2)$  and  $P_1^0 - P_1 = P_1^0 x_2$ . The vapor pressure lowering is defined as  $\Delta P = P_1^0 - P_1$  and will also equal  $P_1^0 x_2$ . For very small temperature changes that are associated with vapor pressure osmometry, it is **assumed** that  $T$ ,  $\Delta H_v$ , and  $p$  are constant. Now, the Clausius-Clapeyron equation [ $dp/dT = (p\Delta H_v)/(RT^2)$ ] can be integrated to yield:

$$\Delta T = [(RT^2)/(p\Delta H_v)] \cdot \Delta P \quad \text{where} \quad \begin{array}{l} p = \text{vapor pressure} \\ T = \text{absolute temperature} \\ \Delta H_v = \text{enthalpy of vaporization} \\ R = \text{gas constant} \end{array}$$

Substitution of the equations yields  $\Delta T = (RT^2 P_1^0 x_2)/(p\Delta H_v)$  and for small pressure changes,  $P_1^0 = p$ , so that  $\Delta T = (RT^2 x_2)/(\Delta H_v)$ . By definition:

$$x_2 = n_2/(n_1 + n_2) \quad \text{where} \quad \begin{array}{l} n_1 = \text{number of moles of solvent} \\ n_2 = \text{number of moles of solute} \end{array}$$

For very small  $n_2$  the relation will reduce to  $n_2/n_1$  and plugging back into the temperature equation gives:



selector, filter, and digital panel meter. Two silicone molded heaters are placed around the cylinder so that they cover about 80% of its surface. A precision controller can control the temperature to a few thousandths of a degree. Coarse and fine controls are calibrated to given temperatures and are set on the control panel.

### **Operational Procedures**

The first step in preparing for a VPO run is to clean the chamber assembly. The chamber is removed from the oven, revealing the baffles, wicks, and thermistors. Gloves should be worn to prevent oils from the hands transferring to the chamber. The platinum gauze coverings of the thermistors are carefully removed with tweezers and placed in a solution of the solvent for which the new samples will be run. The uncovered thermistors and chamber are fully rinsed with the solvent and new wicks placed in the assembly. The chamber is reassembled with the gauze in place and 20 mL of solvent poured into the center cylinder over the thermistors. The injection syringes are then removed, cleaned with solvent, loaded with appropriate solutions or solvents, and returned to the apparatus. The Model 233 is capable of heating the syringes separately from the chamber, but this is seldom used for floor measurements. The temperature control should be set to the appropriate number and the instrument allowed to reach operating temperature. This is usually started before cleaning and allowed to warm and equilibrate for at least one hour.

Calibration with materials of known molecular weight must precede measurement for unknowns to determine the K value. Requirements for standards are vapor pressure no more than 0.1% of that of the solvent, high purity, solubility, and formation of ideal solutions (optional). Sucrose octaacetate is the standard of choice for organic solvents and simple sucrose or mannitol are excellent for aqueous calibration. Sample running is the same for standards and unknowns. Operating temperature for the solvent of choice is determined from a chart in supplied application notes.

Five solutions of the sample are prepared ranging in concentration from 0.7 g/L to 20 g/L based on the expected MW of the sample. The ZERO control on the operating panel is adjusted to get a reading on the meter between 0 and 10. With pure solvent in both syringes, add about

0.03 ml of solvent to both thermistors. This task is simplified by marked screw drives that inject the needles. 0.03 mL will equal 2 full turns of the screws. After each addition, the screws are turned back 1 turn to prevent small drops from falling on the thermistors. Generally, the reading will go off scale and then return to a level value. Adjust the ZERO control to get a reading between 0 and 10 and repeat. Calculate the average value of the trials. The sample syringe is then filled with the most dilute polymer solution and turned until the meter goes off scale, then 30 seconds later, 3 turns. Remember to turn back the screw after each addition. This cleans the thermistor of the previous solution/solvent run. Now, the first real measurement takes place with 2 turns for both the solvent syringe and sample syringe. The voltage is read after stabilization. Three or more trials for the same sample are run and an average calculated. Repeat for each concentration and record. Finally, subtract the pure solvent voltage from these readings to give the true  $\Delta V$  for the various concentrations.

The data is plotted as  $\Delta V/C$  versus  $C$  (g/L) and a best fit straight line is extrapolated to zero concentration. Adjusting our voltage equation for the plot at zero concentration, the following relations are derived:

$$K = \Delta V/C * m_2$$

When using known  $m_2$  to determine  $K$

$$m_2 = (K) / (\Delta V/C)$$

After calibration with unknown  $m_2$  sample

### **MW Ranges for VPO**

If experimental factors are controlled very carefully, very accurate  $M_n$  numbers can be achieved. MW's below 1000 are determinable with a precision of 0.5 %. The lower limit of MW is technically only limited by the vapor pressure of the sample, but useful lower limits are in the 250 level. Upper MW limits as high as 400000 have been reported, but the instrumental sensitivity determines this factor. Most commercial instruments can reach 100000, but it is safest to assume the upper limit as 50000. It should be further noted that the temperature change is inversely proportional to the solvent heat of vaporization. Therefore, benzene and chloroform will have the best sensitivity and water would have the worst. The upper limit for molecular weights in water will be 20000-25000 and this with only the most sensitive instrument.

## **VPO and Membrane Osmometry as Complimentary Methods**

The most obvious comparison of the methods shows that VPO is useful in a lower MW range than membrane osmometry. Membrane osmometry does not require calibration with a molecular weight standard as does vapor pressure osmometry. Determination of property to be measured is the driving force between choice of the two methods. For example, a polymer that is used for injection molding is to be analyzed. The behavior in the molding instrument will depend on the amount of low molecular weight polymer in the material. VPO is the best choice, since membrane osmometry would exclude the low MW portion. On the other hand, a polymer with no low molecular weight polymer present but with additives such as antioxidants or plasticizers would give erroneous  $M_n$  values if VPO was used due to inclusion in the measurement of the additives' MW. Membrane osmometry would be preferred. In an interesting case, polyelectrolytes must be analyzed with a significant amount of electrolyte present to account for their charged behavior. VPO will respond primarily to the salt added and completely eliminate the polymer signal. Membrane osmometry will allow the salt to equilibrate through the membrane and the final osmotic pressure will be due to only the polymer. Using both methods to analyze a possibly highly dispersed polymer will allow a better understanding of the low and high MW ends of the distribution curve.

## **Recent Applications for Combining Osmometry With Other Techniques**

In a recent issue of *Macromolecules*, Lehmann and Kohler reported the use of membrane osmometry as an online detector in correlation with size exclusion chromatography. This allows for absolute molar mass detection. The use of a membrane osmometer as an absolute online detector is important because especially for polar polymers, adsorptive interaction between the column and the polymer in SEC cannot be disregarded. This can cause erroneous results when using the universal calibration technique to determine molecular weight. Colligative properties like osmotic pressure are only sensitive to the number of molecules in solution. Therefore, an absolute SEC calibration can be obtained by a simultaneous measurement of concentration and of a colligative property. In this case membrane osmometry was employed due to its sensitivity.

When the experiments were performed using this technique, the RI detector of the SEC setup was replaced with a membrane osmometer.

The authors redesigned the osmometer because a cell with a flat membrane is not suited for a continuous flow operation. They designed an osmometer containing cylindrical symmetry which contains a semipermeable membrane and an outer glass tube. The polymer solution then flows through the bore of the membrane capillary. The reference cell is filled with solvent and is the volume between the membrane and the outer glass tube. The solution chamber inside the capillary can be easily flushed, ideally suiting it for use as a flow cell and the balloon effect is negligible. The semipermeable support membrane is a highly asymmetric poly(acrylonitrile) hollow fiber which contains an inner separating layer. The inner side or solution side of the support membrane is coated with a dilute solution of poly(dimethylsiloxane). This composite membrane is perfectly suited for online detection because of its mechanical stiffness, high solvent permeability, and low molar mass cutoff. The membrane osmometer and membrane combined, meet the requirements for online detection: low cell volume, short response time, and low molar mass cutoff.

The instrument was tested on both batch and continuous flow operations with poly(styrene) standards. The results were in agreement with the suggested molar masses. Response time is very short in comparison to a standard membrane osmometer and this leads to slight peak broadening. The problems that the authors find need more work are reduction of this peak broadening and a reduction of the pressure noise level along with the elimination of long term baseline drifts. However, this technique has been shown to successfully measure absolute molecular weights by the combination of size exclusion chromatography with online detection using membrane osmometry.

## References

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