Chapter 5

Colligative Properties

5.1 Introduction

Properties of solutions that depend on the number of molecules present and not on the kind of molecules are called colligative properties. These properties include boiling point elevation, freezing point depression, and osmotic pressure. Historically, colligative properties have been one means for determining the molecular weight of unknown compounds. In this chapter we discuss using colligative properties to measure the molecular weight of polymers. Because colligative properties depend on the number of molecules, we expect, and will show, that colligative property experiments give a number average molecular weight.

5.2 Boiling Point Elevation

Figure 5.1 shows the vapor pressure of a liquid for pure liquid and for a solution with that liquid as the solvent. In an ideal solution, the vapor pressure of the solvent, P_A, is reduced from the vapor pressure of a pure liquid, P_A°, to $X_A P_A^\circ$ where X_A is the mole fraction of liquid A. This reduction is reflected in a shift to the right of the vapor-pressure curves in Fig. 5.1. By definition, boiling point is the temperature at which the vapor pressure of the liquid reaches 1 atm. Thus, the right-shift caused by the dissolution of component B in solvent A causes the boiling point to increase. This increase, ΔT_b, is the boiling point elevation effect.

A well known result from introductory chemistry is that the boiling point elevation is proportional to the molar concentration of solute particles

$$\Delta T_b = K_b m \tag{5.1}$$

where m is the molality of solute molecules and K_b is the boiling point elevation coefficient that is a function of only the solvent. Molality is the number of moles of component B per 1000 grams of solvent. If we prepare a solution of an unknown compound of molecular weight B at a concentration

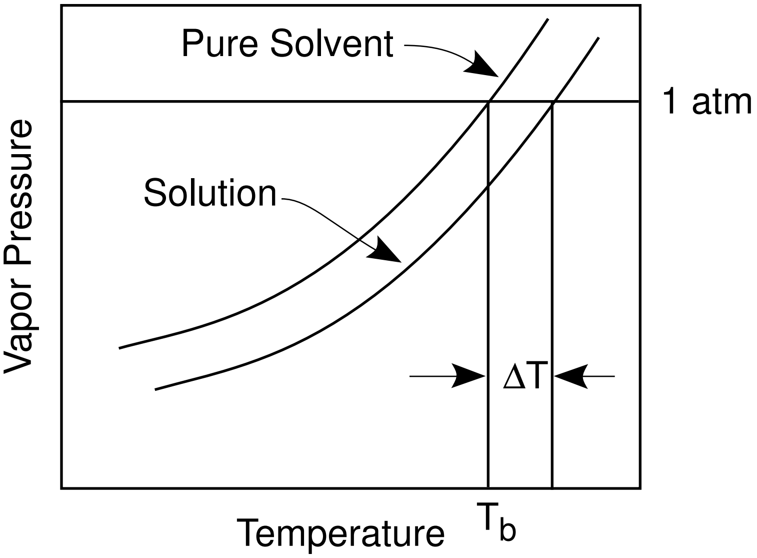

Figure 5.1: Boiling point elevation effect is a consequence of the effect of solute molecules on the vapor pressure of the solvent.

c in g/cm^3, then

$$m = \frac{1000c}{M_B\rho} \tag{5.2}$$

where ρ is the density of the solvent (in g/cm^3). Substituting into the expression for ΔT_b gives

$$M_B = \frac{1000K_b c}{\rho\Delta T_b} \tag{5.3}$$

or

$$\frac{\Delta T_b}{c} = \frac{1000K_b}{\rho M_B} \tag{5.4}$$

For a given solvent (*e.g.*, water where $K_b = 0.52$ and $\rho = 1.00$) and concentration (c), all terms in Eq. (5.4) are known except for M_B. Thus, measuring ΔT_b can be used to determine the molecular weight M_B.

We can also express boiling point elevation in terms of mole fraction. Mole fraction is

$$X_B = \frac{\frac{cV}{M_B}}{\frac{\rho V}{M_A} + \frac{cV}{M_B}} \approx \frac{cM_A}{\rho M_B} \tag{5.5}$$

where V is total volume and M_A is molecular weight of the solvent. The boiling point elevation becomes

$$\Delta T_b = \frac{1000K_b}{M_A} X_B \tag{5.6}$$

To apply boiling point elevation to polymers, we begin by using solution thermodynamics to derive an expression for ΔT_b. At equilibrium, the chemical potential of the vapor is equal to the chemical potential of the liquid

$$\mu_A^{vap} = \mu_A^{liq} = \mu_A^\circ + RT\ln X_A \qquad \text{or} \qquad \frac{\mu_A^{vap} - \mu_A^\circ}{RT} = \ln X_A \tag{5.7}$$

where we have assumed an ideal solution. Differentiating both sides gives

$$\frac{\partial\left(\frac{\mu_A}{T}\right)}{\partial T} = \frac{\partial\left(\frac{G_A}{T}\right)}{\partial T} = \frac{1}{T}\left(\frac{\partial G_A}{\partial T}\right)_P - \frac{G_A}{T^2} = -\frac{S_A}{T} - \frac{H_A}{T^2} + \frac{S_A}{T} = -\frac{H_A}{T^2} \tag{5.8}$$

which is used to get

$$-\frac{H_A^{vap} - H_A^\circ}{RT^2} = \frac{d}{dT}\ln X_A \tag{5.9}$$

where $H_A^{vap} - H_A^\circ$ is the heat of vaporization of the solvent or ΔH_{vap}.

Now consider the process of forming a solution. As the polymer is added, the mole fraction of A will go from 1 at the start to X_A which is the mole fraction of the final solution. During the process, the boiling point will go from T_b to T where T_b is the boiling point of the pure liquid and T is the boiling point of the solution. Integrating over this process gives

$$-\int_{T_b}^{T} \frac{\Delta H_{vap}}{RT^2} dT = \int_1^{X_A} d\ln X_A \tag{5.10}$$

The integrals are easily evaluated if we assume that ΔH_{vap} is independent of temperature over the small temperature range from T_b to T. The result is

$$\frac{\Delta H_{vap}}{R}\left(\frac{1}{T} - \frac{1}{T_b}\right) = \ln X_A \tag{5.11}$$

We can simplify this result using $\Delta T_b = T - T_b$, $TT_b \approx T_b^2$, and $\ln X_A = \ln(1 - X_B) \approx -X_B$. These simplifications apply when X_B is small (which occurs when the solution is dilute) and when ΔT_b is small. In general, ΔT_b will be small when the solution is dilute. The previous equation simplifies to

$$\frac{\Delta H_{vap}\Delta T_b}{RT_b^2} = X_B \tag{5.12}$$

or

$$\Delta T_b = \frac{RT_b^2}{\Delta H_{vap}} X_B \tag{5.13}$$

Comparison of this result to Eq. (5.6) gives a theoretical expression of K_b:

$$K_b = \frac{M_A R T_b^2}{1000\Delta H_{vap}} \tag{5.14}$$

The result is often derived in physical chemistry books.

In applying boiling point elevation to polymer solutions, we should realize that polymer solutions are really solutions of many components. The various components are the polymer species of different molecular weights. Because boiling point elevation is a colligative property, we can write the boiling point elevation of a polymer solution as a sum over the mole fractions of each molecular weight component:

$$\frac{\Delta H_{vap}\Delta T_b}{RT_b^2} = \sum_i X_i \tag{5.15}$$

where X_i is the mole fraction of polymer with molecular weight M_i. We more conveniently rewrite X_i in terms of concentration:

$$X_i = \frac{\frac{c_iV}{M_i}}{\frac{\rho V}{M_A} + \sum_i \frac{c_iV}{M_i}} \approx \frac{c_iM_A}{\rho M_i} \tag{5.16}$$

where c_i is the concentration in weight/unit volume (*e.g.*, g/cm^3) of polymer with molecular weight i. The approximation in this expression is valid for dilute solutions in which the number of moles of solvent is much greater than the total number of moles of polymer. Summing the mole fractions, X_i, results in

$$\sum_i X_i = \frac{cM_A}{\rho}\frac{\sum_i \frac{c_i}{M_i}}{\sum_i c_i} = \frac{cM_A}{\rho}\sum_i \frac{w_i}{M_i} = \frac{cM_A}{\rho\overline{M_N}} \tag{5.17}$$

where

$$c = \sum_i c_i \tag{5.18}$$

The final expression for the boiling point elevation becomes

$$\frac{\Delta T_b}{c} = \frac{M_ART_b^2}{\rho\Delta H_{vap}\overline{M_N}} \tag{5.19}$$

It is common to express the boiling point elevation in terms of the latent heat of vaporization, l_{vap}, defined as energy or vaporization per unit weight or

$$l_{vap} = \frac{\Delta H_{vap}}{M_A} = \frac{\text{J/mole}}{\text{g/mole}} = \text{heat of vaporization in J/g} \tag{5.20}$$

The boiling point elevation becomes

$$\frac{\Delta T_b}{c} = \frac{RT_b^2}{\rho l_{vap}\overline{M_N}} \tag{5.21}$$

Except for incorporation of polydispersity, there is nothing new about the boiling point elevation expression for polymer solutions *vs.* the comparable expression for small molecule solutions. In polymers, however, the solution is more likely to be non-ideal. For this equation to apply we will probably need to use very low concentrations or techniques to extrapolate to very low concentrations.

For an example, let's consider a solution of polystyrene in benzene. For benzene $\rho = 0.8787$ g/cm^3, $T_b = 55$°C, and $l_{vap} = 104$ cal/g. We assume a relatively concentrated solution of $c = 1$ g/cm^3 of a polymer with molecular weight $\overline{M_N} = 20,000$. The change in the boiling point elevation for this solution is $\Delta T_b = 1.4 \times 10^{-3}$ °C. This boiling point elevation is very small. It is probably beyond the accuracy of most temperature measuring equipment. The small change arises despite relatively ideal conditions of a fairly concentrated solution and a low molecular weight polymer. More dilute solutions or higher molecular weight polymers would give an even smaller ΔT_b. The problem with polymer solutions is that for a given weight of material, the polymer solution will have many less molecules than the comparable small molecule solution. When there are a small number of molecules, the change in boiling point (a colligative property) is small. The problem with the boiling point elevation method applied to polymer solutions is that it is not sensitive enough. It has found some use with polymers but it is limited to polymers with relatively low molecular weights. (*e.g.*, $\overline{M_N}$ less than 20,000 g/mol).

5.3 Freezing Point Depression

A similar analysis (but with sign changes) can be applied to the freezing point depression of a polymer solution. The final result is

$$\frac{\Delta T_f}{c} = \frac{RT_f^2}{\rho l_f \overline{M_N}} \tag{5.22}$$

where T_f is the freezing point of the solvent and l_f is the latent heat of fusion. We consider the same example of polystyrene in benzene with $T_f = 5.5°\text{C}$, $l_f = 30.45$ cal/g for the freezing point of benzene. For a $c = 1$ g/cm^3 solution of polystyrene with molecular weight $\overline{M_N} = 20,000$, the change in the freezing point of the solution is $\Delta T_f = 2.9 \times 10^{-3}$ °C. Like the boiling point elevation effect, the freezing point depression effect is too small. The technique is insensitive and only useful for low molecular weight polymer (*e.g.*, $\overline{M_N}$ less than 20,000 g/mol).

5.4 Osmotic Pressure

Another colligative property is osmotic pressure. Figure 5.2 illustrates the osmotic pressure effect. Imagine a pure solvent and a solution separated by a semipermeable membrane. An ideal semipermeable membrane will allow the solvent molecules to pass but prevent the solute molecules (polymer molecules) from passing. The different concentrations on the two sides of the membrane will cause an initial difference in chemical potential. At equilibrium, this difference in potential will be counteracted by an effective pressure across the membrane. As shown in Fig. 5.2, it can be imagined that solvent molecules pass from the pure solvent side to the solution side. The excess height in the column of liquid above the solution side is related to the osmotic pressure by $\pi = \rho g h$. Here π is the osmotic pressure, ρ is the density of the solution, g is the acceleration of gravity (9.81 m/sec^2) and h is the height of the column of liquid.

We begin with a thermodynamic analysis of osmotic pressure. At equilibrium the chemical potential in the solution will be equal to the chemical potential in the pure solvent:

$$\mu_A^{solvent} = \mu_A^{solution} = \mu_A^\circ + RT \ln a_A \tag{5.23}$$

where $\mu_A^{solvent}$ is the chemical potential of the pure liquid or

$$\mu_A^{solvent} = \mu_A^\circ \tag{5.24}$$

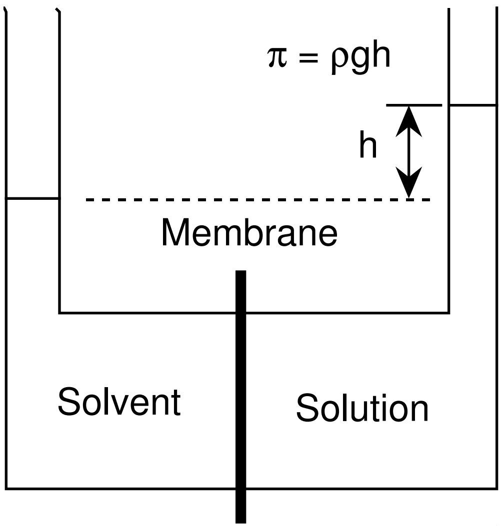

Figure 5.2: A schematic view of osmotic pressure across a semipermeable membrane.

The only way the chemical potentials will be equal will be if the activity of component A in the solution is equal to 1. The activity can be raised to 1 by applying pressure. That is, activity is a pressure dependent quantity. By applying the correct pressure, the osmotic pressure, the activity in the solution can be changed to 1. The osmotic pressure that gets applied occurs naturally by the tendency to approach equilibrium.

To get the pressure dependence of activity, we consider the pressure dependence of the chemical potential

$$\frac{d\mu_A}{dP} = \frac{d}{dP}\frac{dG}{dn_A} = \frac{d}{dn_A}\frac{dG}{dP} = \frac{dV}{dn_A} = V_A = RT\frac{d}{dP}\ln a_A \tag{5.25}$$

Rearranging and integrating the left hand side from the original activity a_A to the final activity 1 and the right hand side from the initial pressure 0 to the final pressure — the osmotic pressure π — results in:

$$\int_{a_A}^{1} d\ln a_A = \int_0^{\pi} \frac{V_A}{RT} dP \tag{5.26}$$

which integrates to

$$-\ln a_A = \frac{\pi V_A}{RT} \tag{5.27}$$

Now, in an ideal solution

$$-\ln a_A = -\ln X_A \approx X_B. \tag{5.28}$$

This last approximation follows because $\ln(1-x) \approx -x$ for small x. Finally, as in the analysis of boiling point elevation, we replace X_B by $\sum_i X_i$ which was derived in Eq. (5.17) to be

$$\sum_i X_i = \frac{cM_A}{\rho \overline{M_N}} \tag{5.29}$$

giving

$$\frac{cM_A}{\rho \overline{M_N}} = \frac{\pi V_A}{RT} \tag{5.30}$$

But, M_A/ρ is the grams per mole of solvent divided by the grams per cm^3 of solvent. The grams cancel and we have cm^3 per mole of the solvent or the partial molar volume of component A — V_A. Substituting into the osmotic pressure equation thus gives:

$$\frac{\pi}{c} = \frac{RT}{\overline{M_N}} \tag{5.31}$$

Rewriting the osmotic pressure equation gives a result that is similar to the ideal gas law

$$cRT = \pi \frac{\sum_i N_i M_i}{\sum_i N_i} \qquad \text{or} \qquad \frac{\sum_i N_i M_i}{V} RT = \pi \frac{\sum_i N_i M_i}{\sum_i N_i} \tag{5.32}$$

which simplifies to

$$\pi V = \sum_i N_i RT \qquad (i.e.\ \ PV = nRT) \tag{5.33}$$

For an example, let's consider the solution of polystyrene in benzene that was used for examples of boiling point elevation and freezing point depression; *i.e.*, a solution of polystyrene in benzene with $\overline{M_N} = 20,000$ and a concentration of $c = 1$ g/cm^3. For the correct units we use $R = 8.3143 \times 10^7$ ergs/K/mol and calculate $\pi = 1.24 \times 10^4$ dynes/cm^2. This pressure will be measured by a difference in heights of liquids in columns. The height difference comes from $\pi = \rho g h$ or

$$h = \frac{1.24 \times 10^4 \text{ dynes/cm}^2}{0.8787 \text{ g/cm}^3 \ 981 \text{ cm/sec}^2} = 14.3 \text{ cm} \tag{5.34}$$

This height difference is large and is an easily measurable quantity. In fact we expect to be able to measure distances at least 100 times smaller than this result. Thus osmotic pressure can, in principle, be used to determine molecular weights in polymers with $\overline{M_N}$ up to 2,000,000 g/mol.

5.5 Practical Aspects of Osmotic Pressure

Osmotic pressure measurements appear to be a suitable method for measuring number average molecular weights in polymers. It is therefore worthwhile considering practical aspects of polymer characterization by osmotic pressure. The first practical consideration is that we expect polymer solutions to deviate from ideal behavior and thus the osmotic pressure expression will need to be corrected. In the limit of zero concentration, the solution will eventually become ideal. We can therefore take a series of measurements and extrapolate back to zero concentration to get the ideal result. In other words

$$\lim_{c \to 0} \frac{\pi}{c} = \frac{RT}{\overline{M_N}} \tag{5.35}$$

The question which remains is "how do we extrapolate?" A common approach in thermodynamics is to use a virial expansion. We thus write $\frac{\pi}{c}$ as a sum of many terms:

$$\frac{\pi}{c} = \frac{RT}{\overline{M_N}} + RTA_2c + RTA_3c^2 + \cdots \tag{5.36}$$

or

$$\frac{\pi}{c} = \frac{RT}{\overline{M_N}}\left(1 + \Gamma_2 c + \Gamma_3 c^2 + \cdots\right) \tag{5.37}$$

Here A_2, A_3, ... and the related Γ_2, Γ_3, ... are called the virial coefficients. If we include enough virial coefficients we will always be able fit experimental data. But, how many of these terms do we need? Furthermore, how do we analyze experimental data when virial expansion terms are required? We consider two approaches to this problem.

In the first approach, we assume that only the second virial coefficient — A_2 or Γ_2 — will be needed. Then π/c is predicted to be linear in concentration:

$$\frac{\pi}{c} = \frac{RT}{\overline{M_N}} + RTA_2 c \tag{5.38}$$

A set of data for π/c *vs.* c can be plotted. If the results are linear, the assumption in the first approach is valid. When the data is linear, the intercept of the data at zero concentration will be $RT/\overline{M_N}$ and thus can be used to determine $\overline{M_N}$.

Besides an intercept, we can measure the slope which is equal to RTA_2. In other words the slope of the π/c *vs.* c plot is proportional to the second virial coefficient — A_2. We can make use of the Flory-Huggins theory to get a physical interpretation of the second virial coefficient. The Flory-Huggins theory includes non-ideal interactions through the Flory interaction parameter, χ. Let's use the Flory-Huggins theory to develop an osmotic pressure theory for nonideal solutions. We begin with an early osmotic pressure formula:

$$\pi = -\frac{RT\ln a_A}{V_A} = -\frac{\mu_A - \mu_A^\circ}{V_A} \tag{5.39}$$

The term $\mu_A - \mu_A^\circ$ is found by differentiating the free energy of mixing

$$\frac{d\Delta G_{mix}}{dn_A} = \mu_A - \mu_A^\circ \tag{5.40}$$

To use the Flory-Huggins theory we differentiate the ΔG_{mix} from that theory. In performing the integration we must realize that v_A and v_B also depend on n_A. The work is left as an exercise to the reader. The result is

$$\mu_A - \mu_A^\circ = RT\left[\ln v_A + \left(1 - \frac{1}{x}\right)v_B + \chi v_B^2\right] \tag{5.41}$$

Substituting into the osmotic pressure formula and at the same time using the approximation $\ln v_A = \ln(1 - v_B) \approx -v_B + v_B^2/2$ (Note that in this approximation to $\ln(1 - v_B)$ we keep one more term than we have used in the past. The reason for the extra term is that the $\mu_A - \mu_A^\circ$ expression already includes terms with v_B^2), the osmotic pressure becomes:

$$\pi = \frac{RT}{V_A}\left[\frac{v_B}{x} + \left(\frac{1}{2} - \chi\right)v_B^2 + \cdots\right] \tag{5.42}$$

The volume fraction of polymer, v_B, is equal to the concentration of B in g/cm^3 divided by the density of polymer — ρ_B ($v_B = c/\rho_B$). The osmotic pressure is then

$$\frac{\pi}{c} = \frac{RT}{V_A x \rho_B} + \frac{RT}{V_A \rho_B^2}\left(\frac{1}{2} - \chi\right) c + \cdots \tag{5.43}$$

The first term is the ideal solution result (which can be deduced by noting that $\overline{M_N} = V_B \rho_B$ and $V_B = xV_A$ in the lattice solution model).. The second term, which is proportional to concentration, gives the second virial coefficient

We return now to the slope of the linear fit of π/c *vs.* c which gives the second virial coefficient. From the Flory-Huggins analysis, the second virial coefficient is:

$$A_2 = \frac{1}{V_A \rho_B^2}\left(\frac{1}{2} - \chi\right) \qquad \text{or} \qquad A_2 = \frac{M_0}{\rho_B}\left(\frac{1}{2} - \chi\right) \tag{5.44}$$

where $M_0 = \overline{M_N}/x$ is the monomer molecular weight. When χ is large and negative, the second virial coefficient will be large and positive and the slope of π/c *vs.* c will be large and positive. A negative interaction parameter also implies a favorable interaction (ΔG_{mix} more negative) and therefore a good solvent will give a large positive slope. In fact the slope of the osmotic pressure data can be thought of as a direct measure of the solvent quality — the higher the slope the better the solvent.

The second virial coefficient from the Flory-Huggins result is also proportional to $1/\rho_B$ or rather is proportional to the specific volume of polymer. This result suggests an excluded volume effect. When the excluded volume effect is absent, the solution will act as if the specific volume of the polymer is zero ($1/\rho_B = 0$) and the second virial coefficient will therefore be zero. The excluded volume effect disappears in a theta solvent and as a result the osmotic pressure data slope will be zero in a theta solvent. In other words a theta solvent acts as an ideal solution to fairly high concentrations. The fact that a zero slope is a low slope illustrates a result from earlier in the course — theta solvents in general are not very good solvents. Although working in theta solvents would simplify data analysis (*i.e.*, give results that obey ideal solution laws) the fact that theta solvents are poor solvents makes working with them difficult. It is usually more convenient to work in good solvents and make use of extrapolation techniques. The observation of zero slope in osmotic pressure data, however, is a useful method for determining theta solvent conditions.

Unfortunately, plots of π/c *vs.* c are often not linear. We thus need a second approach to analysis of data from nonideal solutions. The obvious approach is to include both the second and the third virial coefficients. In other words we assume that deviations from linearity are caused by the third virial coefficient no longer being insignificant. Let's take g as the ratio of the third virial coefficient to the second virial coefficient squared ($\Gamma_3 = g\Gamma_2^2$) and let's ignore terms beyond the third virial coefficient. Then π/c becomes

$$\frac{\pi}{c} = \frac{RT}{\overline{M_N}}\left(1 + \Gamma_2 c + g\Gamma_2^2 c^2\right) \tag{5.45}$$

We now have two parameters — Γ_2 and g. Deriving two parameters for osmotic pressure data will be more complicated than deriving the slope and intercept of simple linear fits. It requires more advanced curve-fitting techniques. We can simplify the process by introducing some theoretical calculations about g. For hard spheres, g can be calculated to be $g = 5/8$. For polymer molecules, g has been estimated to be $g = 0.25$ to 0.28. The actual value of g depends on various properties such as the expansion coefficient α, the characteristic ratio, *etc.*. Fortunately, however, g is restricted to a relatively narrow range for most polymers.

Because g must be positive and a polymer cannot be more impenetrable than hard spheres, g must be between 0 and 5/8. If we pick a value for g than we are left with only one parameter (Γ_2) and we calculate $\overline{M_N}$ and Γ_2 by simpler curve fitting analyses. Fortunately it has been found that the results are not very sensitive to the exact value of g. Because polymers have g's calculated to be near 0.25, we will assume $g = 0.25$. The choice of $g = 0.25$ is desirable because it completes the square and the data analysis can again be done by linear fits (Scientists, especially scientists that worked before computers, like linear theories):

$$\frac{\pi}{c} = \frac{RT}{\overline{M_N}}\left(1 + \Gamma_2 c + \frac{1}{4}\Gamma_2^2 c^2\right) \qquad \text{or} \qquad \sqrt{\frac{\pi}{c}} = \sqrt{\frac{RT}{\overline{M_N}}}\left(1 + \frac{\Gamma_2 c}{2}\right) \tag{5.46}$$

When g can be assumed to be 0.25, a plot of $\sqrt{\pi/c}$ *vs.* c should be linear. The slope will give Γ_2 and the intercept will give $\sqrt{RT/\overline{M_N}}$.

The advantage of setting $g = 0.25$ is that the data can be analyzed with a simple linear fit. This advantage was important before computers were readily available. Now we can easily treat g as a second parameter and do a two parameter fit to the data. You will try this type of analysis in one of the class labs and be able to discuss whether the added complexity improves or weakens the interpretation of the results.

5.6 Experimental Aspects of Membrane Osmometry

A simple type of osmometer is illustrated in Fig. 5.3. The solution is placed in a cell with membranes on either side (one or two membranes, but two gives more area and faster equilibration). The entire assembly is then immersed in pure solvent. The heights of the liquids in the capillaries are read and the height difference gives the osmotic pressure. This apparatus is called a block type osmometer. It is the type of osmometer used to get the data that will be given to you in a lab. This osmometer uses a small cell and a large membrane. The membrane is supported by stainless steel plates with holes. By supporting the membrane, the membrane can be made larger; with larger membrane area equilibrium will be reached sooner.

Block osmometers are called static osmometers because they wait for the natural development of equilibrium. The problem with static osmometers is that it can take hours (12-24 hrs) to reach

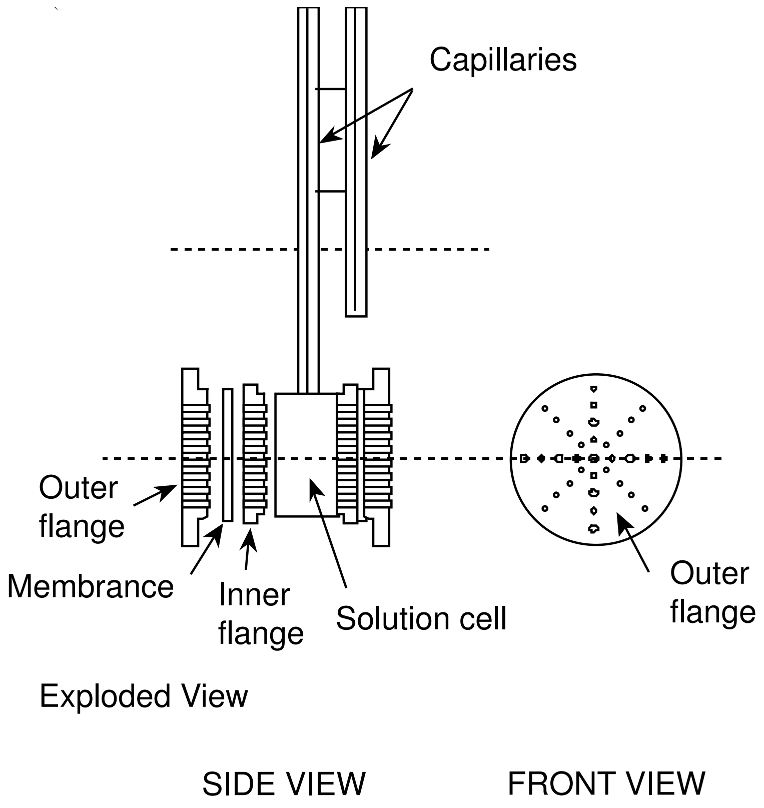

Figure 5.3: A block type, static osmometer.

an accurate equilibrium. The time depends on many factors such as the membrane area and the speed of transport through the membrane. To quicken osmotic pressure experiments, dynamic osmometers are sometimes used. Recall that osmotic pressure develops for the purpose of raising the activity of the solvent in the solution to 1. By applying a pressure it is possible to do the same thing. You will know when you have applied the correct pressure by monitoring flow across the membrane. When you apply enough pressure to stop the flow you have artificially reached equilibrium. The pressure required can be used to get the equilibrium osmotic pressure. This quick method, unfortunately, is less accurate.

Finally, we make a few comments about what makes a good semipermeable membrane. The membrane must be permeable to solvent and impermeable to polymer. This requirement limits the low-end applicability of osmometry to $\overline{M_N}$ of 20,000 g/mol or more. Note that we really require all polymers to be above 20,000 g/mol otherwise the low molecular weight tail will pass through membrane and the measured $\overline{M_N}$ will be too high (do you see why it would be too high?). Therefore, polydisperse polymers probably require $\overline{M_N}$ greater than about 50,000 g/mol; for monodisperse polymers it might be possible to go down to 20,000 g/mol.

There are also some material concerns for the membrane. An obvious concern is that the membrane not be soluble in the solvent. Perhaps the most common membrane material is gel cellulose.

Other membranes include cellulose hydrate, cellulose acetate, cellulose nitrate, polyurethanes, and poly(chlorotrifluoroethylene).

Problems

5–1. In analyzing osmotic pressure data why is a plot of $\sqrt{(\pi/c)}$ versus c sometimes used rather than a plot of (π/c) versus c?

5–2. The following are data from osmotic pressure measurements on a solution of polyester in chloroform at 20°C. The results are in terms of centimeters of solvent. The density of $HCCl_3$ is 1.48 g/cm^3. Plot π/c versus c and find $\overline{M_N}$ under the assumption that you can neglect terms beyond the second virial coefficient.

c (g/dl)	h (cm of $HCCl_3$)
0.57	2.829
0.28	1.008
0.17	0.521
0.10	0.275

5–3. a. Suppose that in a different universe that the boiling point elevation was given instead by

$$\frac{\Delta H_{vap}\Delta T_b}{R\Delta T_b^2} = \frac{w_B M_B}{M_0} = \frac{1}{M_0}\sum_i w_i M_i \tag{5.47}$$

where w_i is the weight fraction of polymer with molecular weight M_i and M_0 is the monomer molecular weight. By this law, what molecular weight average could by found from boiling point elevation measurements and give a formula for calculating that molecular weight average.

b. The measurement of boiling point elevation is not very useful for finding the molecular weight of high molecular weight polymers. If boiling point elevation was given instead by the formula in part a, would it be a more or less useful approach to finding the molecular weight of high molecular weight materials?