

Osmotic pressure and polymer molecular weight determination

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Goal: The molecular weight of a polymer is determined by analyzing osmotic pressure data.

Prerequisites: An introductory knowledge of ideal versus non-ideal solution behavior and colligative properties.

Resources you will need: This exercise should be carried out within a software environment that can generate a best-fit line for an x - y data set. The software should also report uncertainties in the determined slope and y -intercept. You will also be graphing the data along with the fitted function.

Background:

Suppose you are given an unknown biomolecular substance, such as a protein, RNA strand, or polysaccharide, and you are then asked to determine the molecular weight of the substance. What experimental methods are available for determining the molecular weight of a large molecule (or perhaps a synthetic polymer or biopolymer)?

One of the more precise techniques involves the measurement of osmotic pressure. The instrument for carrying out these measurements is called an osmometer. The device consists of a semipermeable membrane that separates two solution compartments. The semipermeable membrane is made of a material that permeates the solvent (not the solute). If the membrane separates pure solvent from a solution, an osmotic pressure exists across the membrane which, in turn, drives the flow of solvent through the membrane from the pure solvent compartment to the solution compartment. The flow of solvent that occurs due to a concentration gradient across the membrane is called osmosis.

Osmotic pressure is a colligative property, which means that it is proportional to the concentration of solute. The van't Hoff equation is often presented in introductory chemistry for calculating osmotic pressure (Π) from the moles of solute (n_{solute}) that occupy a given volume (V) and the absolute temperature (T) of the solution;

$$\Pi = \frac{n_{\text{solute}}RT}{V} \quad (1)$$

Note the similarity between equation (1) and the ideal gas equation ($P=nRT/V$). But just like the ideal gas equation, the van't Hoff equation is only valid for an ideal system. In this case, equation (1) is only valid for an ideal solution, which is a hypothetical solution in which the solute-solvent, solvent-solvent, and solute-solute interactions are all equivalent. Since all non-volatile, non-electrolytic solutions approach ideal behavior in the dilute limit, equation (1) is actually a limiting law, and should be written in the form

$$\lim_{n_{\text{solute}} \rightarrow 0} \Pi = \frac{n_{\text{solute}}RT}{V} \quad (2)$$

When using an osmometer, it is more convenient to express concentration in terms of the 'grams' of solute per liter,

$$c = \frac{g}{L},$$

whereby we can make the following substitution in equation (2):

$$\frac{n_{\text{solute}}}{V} = \frac{c}{M},$$

where M is the molecular weight of the solute. In this fashion, and with minor rearrangement, equation (2) can be written as

$$\lim_{c \rightarrow 0} \frac{\Pi}{c} = \frac{RT}{M}. \quad (3)$$

According to equation (3), the molecular weight of a solute can be obtained by plotting osmotic pressure divided by c versus concentration and extrapolating the data back to $c = 0$.

Since equation (3) is only exact in the dilute limit, we can recognize this relationship as the first term in a more general power series expansion in c ,

$$\frac{\Pi}{c} = RT \left(\frac{1}{M} + A_2 c + A_3 c^2 + \dots \right), \quad (4)$$

where A_2 and A_3 are called the second and third virial coefficients, respectively. These coefficients are empirically determined constants for a given solute-solvent system, and also depend on temperature. According to statistical mechanical solution theory, A_2 represents the interaction of a single solute particle with the solvent, and higher order virial coefficients are associated with correspondingly larger number solute particle cluster interactions with the solvent.

The value of A_2 is of practical importance to those who are interested in working with a particular solute-solvent system. A negative value of A_2 is indicative of a 'good solvent' (i.e. the solute will be highly soluble in the solvent due to favorable solute-solvent intermolecular interactions). A positive value of A_2 indicates the solute is insoluble in the solvent. Since A_2 is temperature dependent, there will exist a special temperature for each solute-solvent system where $A_2 = 0$. This temperature is called the Flory Θ -temperature, and represents the theoretical temperature at which an infinite molecular weight solute just precipitates from solution. When a solvent has a Flory Θ -temperature that lies somewhere between ambient to slightly elevated temperature conditions, then that solvent is often referred to as a ' Θ -solvent' for that solute. Among other things, saying that a solvent is a ' Θ -solvent' implies that it is a great solvent for recrystallizing the solute (for purification purposes).

In this exercise, you will be given the osmotic pressure of a polymer solution, cellulose tricaproate in dimethylformamide, over a range of concentrations and at three different temperatures. You will determine the molecular weight (M) of the polymer, the second virial coefficient (A_2) at each temperature, and the Flory Θ -temperature for this system.

Experimental Data:

Cellulose is a natural polymer that makes up nearly 80% of all the biomass on earth (cotton is nearly 100% cellulose). Structurally, cellulose is a linear chain of glucose monomers, linked together at the 1,4 positions of the glucose ring. These glucose chains can be hundreds of units long, and the corresponding molecular weights of these polymers can be several hundred thousand grams per mole.

The following table contains osmotic pressure data at three different temperatures for a cellulose derivative called 'cellulose tricaproate' dissolved in dimethylformamide at a number of concentrations. The data was obtained from Krigbaum, W.R. and Sperling, L.H. *Journal of Physical Chemistry*, **64**, 99 (1960).

<u>Concentration (c) - (g/L)</u>	<u>Osmotic pressure at 30.0°C - (atm)</u>	<u>Osmotic pressure at 41.6°C - (atm)</u>	<u>Osmotic pressure at 53.5°C - (atm)</u>
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2.7	0.00046	0.00052	0.00061
12.5	0.00210	0.00248	0.00293
17.0	0.00265	0.00343	0.00384
22.0	0.00323	0.00442	0.00543

Exercise:

1. Calculate Π/c for each of the three data sets. Using an appropriate software environment, plot Π/c versus c and determine the best-fit line for each data set. By fitting our data to a line, we are assuming that terms higher than the second virial coefficient in equation (4) are negligible. Determine a value for the molecular weight (M) of the polymer and A_2 at each temperature (NOTE: report the second virial coefficient in units of (mol·ml)/g², which are the units most commonly utilized in practice).
2. Of course, the molecular weight (M) should not depend upon temperature. Does your determined values of M vary significantly over the three temperatures investigated here (When answering, you should consider the uncertainty in the y -intercept of your best-fit lines).
3. Based upon the values of A_2 that you obtained, is dimethylformamide a 'better' solvent for cellulose tricaproate at lower or higher temperatures? Plot your three A_2 values against temperature and estimate the Flory Θ -temperature for this system.

Suggestions for improving this web site are welcome. You are also encouraged to submit your own data-driven exercise to this web archive. All inquiries should be directed to the curator: Tandy Grubbs, Department of Chemistry, Unit 8271, Stetson University, DeLand, FL 32720.

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