

Differential Index of Refraction, dn/dc

Introduction

Following concentration fluctuations with light scattering turns out to be a great way to obtain thermodynamic information about polymeric and colloidal systems. Effectively, the tiny concentration fluctuations that occur spontaneously provide the same osmotic pressure information as a large, forced gradient imposed by a semipermeable membrane in a real osmometer. To unlock that information one needs a key: the specific refractive index increment, usually called dn/dc but sometimes given the symbol ν and called the specific refractive index increment.

dn/dc is how much the refractive index of a solution varies for a given increment in concentration, expressed as g/mL

$$\nu = \left. \frac{dn}{dc} \right|_{c=0} = \lim_{c \rightarrow 0} \left(\frac{n - n_0}{c} \right)$$

Clearly, dn/dc has the units of mL/g since refractive index, n , is a pure number. We can also guess that dn/dc is generally a small number. For example, poly(methylmethacrylate) has a refractive index in its pure state of about 1.5 and a density of about 1 g/mL. The refractive index of a typical solvent (say, THF) is about 1.4. A ballpark figure for dn/dc is, therefore, $(1.5-1.4)/(1 \text{ g-mL}^{-1}) \cong 0.1 \text{ mL/g}$.

At least one huge table of specific refractive index increments has been compiled (Huglin). For fun, look into Huglin and see how far off our estimate of dn/dc for PMMA in THF is. These old values are very reliable, but there is one problem: they are often at mercury lamp wavelengths instead of the usual laser wavelengths we want today. That isn't too bad, because ν usually varies only weakly with wavelength λ_0 . If ν was measured at two or more wavelengths, merely construct a plot of ν vs. $(\lambda_0)^{-2}$. This "Cauchy plot" will be a straight line from which you can extract ν at any wavelength you need. You may also need to correct literature data for temperature. Both wavelength and temperature corrections are discussed in Huglin.

Instruments

We just showed that *replacing* the solvent with the polymer corresponds to a $\Delta n \cong 0.1$. Normally, we use dilute solutions--say 0.1% $\cong 1 \text{ mg/mL}$. So the change Δn between solvent and solution is very small: $0.001 * 0.1 \cong 10^{-4}$. Normal refractometers of the type one would use to check the purity of an organic liquid are barely precise enough to see these small differences between solvent and solution. At this level of precision, temperature drift becomes a serious concern. We need a *differential* refractometer, a device that directly looks at pure solvent *and* the solution at the same time and responds to the *difference* in their refractive index. Decent temperature control is still needed, but

the requirements are much less stringent: temperature drift simultaneously affects both solvent and dilute solution about the same amount. The effects nearly cancel.

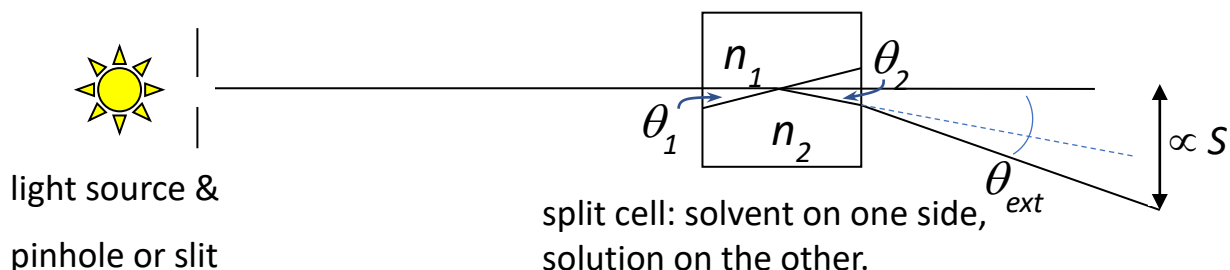
The LSU Polymer Analysis Laboratory operates a total of 5 separate instruments. Two of these are "stand-alone", "batch" instruments. The other three are attached to GPC's and operate as flow cells.

- Brice-Phoenix, a batch instrument. Almost four feet long, the classic BP is built on a rigid lathe bed. Its 1953 design (and probable 1960's construction) is still very serviceable. If you do not obtain straight lines with correlation coefficient $r > 0.9999$ you did something wrong!
- Debbie's Tipton's machine, a batch instrument. A kind of electronic version of the BP inspired by the 1994 paper of Wu and Xia, the "DT" instrument was built in 1997 with help from the LSU shops by Russo Ph.D. student Debbie Tipton, then a consultant for Albemarle. When Debbie took a job at Chevron, the instrument was donated to LSU. This machine is probably easier to use than the BP but not as precise (r may "only" contain three 9's).
- Waters DRI's on the aqueous and non-aqueous GPC's; flow instrument.
- A third DRI from Professor Spivak; flow instrument.

Many other instruments have been constructed elsewhere. The description in Huglin seems thorough for the older instruments (Huglin's description of the BP is particularly comical if you don't mind insults to American culture dished out with dry British humor). More recently, very, very precise instruments have been built using interferometric principles (the Wyatt Optilab, for example).

Principles of Operation

Most instruments are basically the same. Each has a split cell, or "crystal" with two compartments--one for solvent and one for solution. These are separated by a transparent glass wall, canted at an angle from the incident beam. Light traversing the cell deflects a tiny amount according to Snell's law. Subsequent optical elements, and the cell-air interface itself, convert this to a displacement that is proportional to the difference, $\Delta n = n - n_0$, between the solution and solvent refractive index. In the BP, the beam displacement is measured visually with the aid of a microscope. The other instruments obtain this deflection electronically using PSD's (position sensitive detectors).



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Calibration

It is always necessary to calibrate the instrument's response. The goal is to know how some response parameter S (for signal) varies with Δn . S might indicate a voltage in the electronic machines, or a "dial reading" in the BP. The machines are all exquisitely linear (you are about to measure the straightest lines of your scientific career!) so we can safely write:

$$S = O + \frac{dV}{dn} \Delta n$$

Where O represents an offset and V stands for voltage (electronic instruments) or visual (on the BP, where one directly views the deflection).

You want the slope, dV/dn . To get it, make up solutions with known Δn . How? Well, very careful measurements of dn/dc have been made on salt solutions. Here are some of the values at different wavelengths.

$\lambda_o/\text{\AA}$	Light Source, color	dn/dc in mL/g for KCl /H ₂ O @ 25°C	dn/dc in mL/g for NaCl /H ₂ O @ 25°C
6328	Helium-neon laser, red	0.13182	0.17010
5890	Sodium lamp D line, orange	0.13277	0.17138
5145	Argon ion laser, strongest green	0.13496	0.17435
4880	Argon ion laser, strongest blue	0.13599	0.17575

Table 1. Salt solution data for calibration of refractometers. These data represent the Tahir Jamil rework of Mark DeLong's analysis of the original BP data, which used Cauchy plots to perform extrapolations & interpolations of the available Hg-line data.

Other values are known (example: dn/dc of Dow polystyrene 1683 in THF = 0.185 mL/g for red light). The way to get Δn is to prepare aqueous solutions using careful quantitative analytical chemistry techniques (i.e., 4- or 5- place precision, adequate mixing, quantitative transfer). The salts are carefully dried to constant weight at modest temperatures (~100 °C). Temperature is controlled to 25.0 °C. Then:

$$\Delta n = c \cdot \frac{dn}{dc}$$

So you measure the response S vs. Δn for each of several concentrations, and then plot S vs. Δn . The slope is dV/dn and you don't care about the offset, O .

For the flow cell DRI's on the GPC instruments, it is also possible to calibrate using an integral method. See the [GPC/LS HowTo](#) for information about this.

Measurements

With dV/dn in hand, you can move ahead to measurements of your polymer unknown. You again need a set of precisely made solutions. Insert each seriatim into the split cell, using solvent as the reference. Start with solvent vs. solvent (what's our motto again?--"Measure Nothing First"). Ascend to progressively higher polymer concentrations. Measure and plot S vs. c ; the slope is dV/dc and you obtain dn/dc for your unknown by ratio:

$$\frac{dn}{dc} = \frac{(dV/dc)}{(dV/dn)} = \frac{\text{slope of measurement plot}}{\text{slope of calibration plot}}$$

Exercise: what is the expectation for the uncertainty of dn/dc in terms of the dV/dc and dV/dn uncertainties?

General Specifics (Ha! The joys of writing without benefit of an editor.)

OK--so getting dn/dc is easy in principle. Still, there are questions and considerations. Some of these apply primarily to the "batch" machines (BP and DT).

- Regardless of the temperature at which you wish to measure your polymer, the calibration should be performed at 25°C where Table 1 applies. Check the temperature in the cell with a thermometer--adjust water bath or other heater until desired temperature is reached.
- Despite the split cell, temperature regulation is important. Let the samples equilibrate a fairly long time (observe signals to until steady).
- Be careful about evaporation. Some cells can be capped.
- Don't bump the cells--you will have to start over if you do. Be careful putting samples into and out of the cells.
- Work "up" in concentration from solvent vs. solvent to solvent vs. most concentrated solution. Be sure to rinse the sample chamber with plenty of the new solution when you make changes.
- Take great care not to scratch the insides of the cell when loading solutions. Plastic tips are advisable.
- When done, rinse both sides with fresh solvent. Then work them back by a series of appropriate solvent exchanges to some normal, stable solvent (e.g., water or alcohol). It's OK to leave the cells filled with clean, stable solvent.
- If you have to clean any cell, take great care not to scratch it. Use Kodak optical lens tissue (Kimwipes is NOT, REPEAT NOT, a substitute!). Pat the sample dry, don't rub. See Russo for instructions about removing and cleaning cells. They are expensive and easily damaged.

Specifics by Instrument

Brice-Phoenix: On the BP, your "signal" S is obtained in a crazy way. The cell is rotatable by 180° . You measure in the "D1" and "D2" positions, then subtract. Actually, you also subtract the D1-D2 values for pure solvent (which should be small, since $D1=D2 \cong 5.00$ for solvent vs. solvent; if not the machine needs to be re-aligned).

$$S = (D2-D1)_{\text{sample}} - (D2-D1)_{\text{solvent}}$$

It is very easy to change wavelength on the BP. You might as well go ahead and collect data for all 4 wavelengths provided. You may discover during some future light scattering experiment that you need blue light, not red.

Debbie Tipton: The DT instrument has poor temperature control (any volunteers to work on that?). Otherwise, it works great. Take care not to use too strong a light source. It turns out the Hamamatsu PSD misbehaves when the light is too bright. You will know it easily--there's a deadzone in the center of the PSD. If the light is too bright, moving the spot across its center (e.g., by adjusting the lens transversely) has no effect.

The DRI's: The instructions given above for measurement will work for the DRI's, but reading them involves the GPC software. You can also integrate the signal and more or less invert the calibration procedure given in the GPC/LS handout. Hint: the area under the curve should be proportional to $c \cdot (dn/dc)$ if the injected volume is constant (and if no polymer is adsorbed to the column--a very real danger in some cases!).

Simple Experiments to Learn the Batch Instruments (Brice-Phoenix & Tipton)

Resources needed

- Some cheap, low-M water-soluble polymer (example: ethylene glycol or sodium polystyrene sulfonate).
- Dry KCl
- Ten (10) calibrated 100-mL volumetric flasks, maybe stirbars and stirplate.
- Glass pipets: 10, 20, 50 mL
- Pipet bulb.

Preparing the Polymer.

Vacuum dry the polymer days in advance. As usual, repetitive measurements are needed to ensure that the polymer is really dry (Hint: if it gets significantly *heavier* with time, you may need a new trap on the vacuum pump).

Calibrating the Instrument. For the Brice Phoenix, solutions of about 1% KCl should be used. Higher concentrations (perhaps 3-5%) might be better for the Tipton device, which is less sensitive.

Nominally 1% Polymer Stock Solution (c_{\max}). Weigh 1 g into a 100-mL volumetric flask, using quantitative transfer techniques. (If you don't know what this means, ask). There is nothing magic about the number 1 g, but you *do* want to measure this weight very well. (For 4010 lab, we'll wimp out and use those cruddy organic chem. balances, but in a research measurement, one would use a good analytical balance. One would also calibrate the 100-mL volumetric, but we'll skip that too. If you have never calibrated a 100-mL flask *with buoyancy correction* you may wish to ask us how that is done).

As usual, add only one-third of the required solvent (water) until the polymer dissolves. You can add a magnetic stirbar, but you will have to remove it later (with rinsing to get off any polymer stuck to the stirbar). So you would only do this if necessary.

Add water to the line, cap the flask and turn it upside down (slowly, so the fluid has time to respond) at least 25 times. Many failures can be attributed to solutions that were not allowed enough time or shaking to get homogeneous.

Dilutions. Prepare solutions using glass pipets (e.g. 0.1, 0.2, 0.4 and 0.5 c_{\max} but the exact matrix of solutions is non-critical). As always, try to minimize double-dipping (e.g., the 0.2 c_{\max} solution should not be made from two uses of 10-mL pipets; it would be better to make an 0.25 c_{\max} solution using a 25-mL pipet).

Instrument use. Put solvent (water, usually) in both chambers of the divided cell. Make a reading and note which side contains the water. For the Tipton instrument, it is a good idea to scan the beam across the detector to see there are no "dead spots" (where the signal does not change with beam position). If there is a dead spot, it means the light is too bright. See someone about making it dimmer. Work from low concentrations to high, keeping the solvent on the same side always (just leave it there!). NEVER remove the cells to change a solution. Rather, use a disposable pipet *carefully* to withdraw the previous solution. Rinse with new solution. Remove that, refill and measure. For the Brice-Phoenix, it is a good idea to measure each reading a few times. For the Tipton instrument, you can record the *range* of display values observed over some set time (e.g., 10 s). Be sure to give the samples time for temperature equilibration.

References

M.B. Huglin, in *Light Scattering from Polymer Solutions*, M.B. Huglin, Ed., Academic Press, 1972; Ch. 6.

Brice-Phoenix Manual, available from Prof. Russo. (Original BP manual plus re-works by L. Mark DeLong and Tahir Jamil).

C. Wu and K.-Q. Xia, *Review of Scientific Instruments*, **65(3)**, 587-590, 1994.

