Optical Activity Laboratory

Organic Chemistry Lab: AEMoody

This laboratory will introduce you to basic principles of optical activity and the use of a simple polarimeter; for example, the relationship of the specific rotation, [α], of a molecule to its concentration, c (units: $^{g}/_{mL}$), in solution and the pathlength, l (units: dm), of the solution. (In this equation, θ is the measured rotation (units: degrees.)) Thus, the units of [α] are $\frac{\text{degrees}\cdot\text{mL}}{\text{dm}\cdot\text{g}}$.

$$[\alpha]_{\lambda}^{T} = \frac{\Theta}{l\cdot c}$$

Read about the design of polarimeters in your organic lab textbook, and then read about the design and general use of the simple polarimeter you will use (attached).

Experiment 1. The Relationship Between Optical Activity and Concentration using Sucrose.

- Each of you will be assigned to make one of four aqueous sucrose solutions for your lab bench. These freshly prepared solutions will be shared with the other students at your lab bench. Include a table like the one given here for this data in your notebook.
- To prepare the solutions, pour the water into a 100 mL beaker and add your stir bar. Place the beaker on your stirring hotplate, and stir without heating. Measure the mass of the sucrose that you will use (as accurately as the balance allows) and add it slowly with stirring to the water in the beaker. Allow each small portion to dissolve before adding another small portion. Be patient! This takes longer than you might predict, however all of the sucrose MUST be dissolved before measuring its optical rotation. After it has all dissolved, pour the solution back into your graduated cylinder to determine the Actual Volume. Share this information with the people at your lab bench!

Solution #	~ Mass Sucrose	Actual Mass	~ Vol. Water	Actual Vol.	Conc.
1	~7-9 g		~30.0 mL		
2	~14-16 g		~30.0 mL		
3	~22-24 g		~30.0 mL		
4	~30-32 g		~30.0 mL		

- Prepare a second table for the observed rotation data of these sucrose solutions and for water without sucrose. In this second table, include columns for the sucrose sample concentration, pathlength, actual observed rotation, and corrected observed rotation. All of your measurements must come from a single polarimeter! Record your polarimeter number in your notebook.
- Record the polarimter number and check its zero point by pouring distilled water in the polarimeter cell to a height of 10.0 cm; place the cell in the polarimeter. Properly position the light so that you can see the image of the filament in the eyepiece. Rotate the eyepiece until the image is as completely blocked off as possible. Record this extinction point (the zero point°) as the observed rotation of water in your second table.
- Pour out the distilled water and dry the cell. Using your own sucrose sample, pour the liquid into the polarimeter cell making the pathlength as close to 10.0 cm as possible. Record the exact pathlength. Go through the same process as above. Record the angular reading corresponding to the extinction point as Θ. You will then share this sample cell loaded with your sample with your labmates, and they can use your polarimeter cell in their own polarimeters for their measurements.

- Repeat the previous step with the other sucrose solutions using your labmates' polarimeter cells, but doing the measurements *in your own polarimeter*. After all of the students at your table have measured the observed rotations of each of the four sugar solutions, then they may be poured down the drain. Be sure to wash the polarimeter cells well.
- For each solution, correct the Θ readings for the zero point.
- Make a graph in Excel of the corrected values of Θ as a function of concentration (c); you should include the reading for water as a sucrose concentration of 0.00 g/mL. NOTE: be sure to use the units of grams/mL for concentration! Let the computer compute the best straight line through the data, recording this equation (and the corresponding R^2 value) on the graph.
- Calculate your experimental value for the specific rotation for sucrose using your data and the slope of the straight line on your graph. Be sure to use the correct units!
- Compare this value to the expected value from the literature.

Experiment 2. The Relationship between Optical Activity and Pathlength.

R-(-)-carvone is the primary odor component of spearmint oil. You will have a commercial, technical grade sample of *R*-(-)-carvone in lab. **CAUTION: Even though both *R*-(-)-carvone and *S*-(+)-carvone have been used as flavoring ingredients for consumer products, you should treat these substances with the respect afforded any substances with which you work in the laboratory. Do not allow them to contact your skin, and do not breathe the vapors.**

- Prepare a third table for the data you will collect for this material. It should have columns for your measured pathlengths, the actual observed rotations, and the corrected observed rotations.
- Several cells should be charged with this technical grade *R*-(-)-carvone. Various portions of it are in each cell in order to get different pathlengths; measure each pathlength carefully. Then, measure the rotation of each of the different known pathlengths of *R*-(-)-carvone, using the cells that they are in and using your own polarimeter. Be careful not to spill the material while measuring the exact pathlengths! Replace the *R*-(-)-carvone sample cells for the other students in the lab to use.
- Plot a graph of corrected observed rotation (in degrees) as a function of pathlength (in dm) and fit the data with linear regression, again recording the equation (and its corresponding R^2 value) on your graph.
- From the slope of this line and using the density of carvone as the value of the concentration, calculate the specific rotation of *R*-(-)-carvone.
- Compare this specific rotation with a literature value.

Experiment 3. The Relationship between Optical Activity and Enantiomerism.

S-(+)-carvone is the primary odor component of caraway oil. Again, use the polarimeter cell specifically for this isomer! This material is over three times more expensive than its enantiomer and we MUST keep them separate!

- Measure and record the observed rotation of the provided sample and its pathlength.
- Using just this one set of data, compute the sepcific rotation of the *S*-(+)-carvone.
- Compare the magnitude and direction of this specific rotation with that for *R*-(-)-carvone that you computed above *and* to the literature value. Do not expect exact agreement, since the technical samples of each are not totally pure.

Clean up: Be especially careful to clean your lab benches after this experiment, since spilled sugar will attract insects. All aqueous sucrose solutions can be flused down the drain with lots of water. All carvone samples are reused and should not be discarded by students.

The Design and General Use of Simple Polarimeters

(adapted from I^2R literature)

Many applications of polarimetry do not require the ultimate degree of accuracy, and thus a simple polarimeter can be a very useful tool. One of these applications is the education of students about the topic of optical activity. For this, only a simple, inexpensive, rugged polarimeter is needed. If precision of 0.01° is not required, and precision of 1° is adequate, then a simple polarimeter can be designed with certain other simplifications following: the temperature may be held to the nearest 5° C; instead of an expensive sodium light, a yellow filter and an incandescent or tungsten light with an exposed filament can be used; the pathlength of the light through the solution being studied need only be estimated to the nearest mm. For these simplifications to work well, the polarimeter must be used with solutions that are sufficiently concentrated and optically active so that optical rotations of at least 5 - 15° are observed.

The I^2R polarimeter has optics similar to those of a conventional polarimeter, except that the light path is vertical rather than horizontal or inclined, and the measurements are made at the point of optical extinction rather than the point of maximum brightness. A final point of difference between the I^2R polarimeter and the traditional polarimeter is the use of a Polaroid sheet in the optics instead of the very expensive crystal prisms. This material was developed by E. H. Land, the founder of Polaroid Corporation.

The Qualitative Use of the Polarimeter. Once you have a polarimeter available, the phenomenon of optical rotation is quite easy to demonstrate. First you should look through the eyepiece when the light source is turned on and the cell is empty. If it is an I^2R polarimeter, rotate the eyepiece to the point at which the light, or the image of the filament, is as completely extinct as possible. Note the reading on the rotation scale. (It should be close to zero.) Then pour an aqueous solution of ordinary sugar into the cell. (Approximately ten g of sucrose in 50 mL of water works well.)

You will immediately notice that something has changed when you look through the eyepiece. Now try rotating the eyepiece, clockwise or counterclockwise. You will find that it will be necessary to turn the eyepiece 10° or more clockwise to regain the condition that existed when no solution was in the cell. You are observing the rotation of plane polarized light by the optically active sucrose solution.

Quantitative Measurements: Specific Rotation. If you are now ready to make quantitative measurements, proceed as above, using a sugar solution of known composition. Carefully check the zero point when the liquid cell is empty and again when it contains your solution. The difference between these two readings is called the observed rotation. You should also note carefully the pathlength of the solution through which the plane polarized light is traveling. This optical rotation is a physical property of the particular solution in the cell. It is dependent on the concentration of the optically active substance in the cell, the solvent used, the temperature, the pathlength through which the light traveled, and the wavelength of the light.