Stereochemistry and Polarimetry

Introduction

The concept of stereoisomerism and the handedness of molecules is difficult to grasp in a lecture setting with words alone because stereoisomerism is really best understood by visual perception. Exploration of the concept by means of models and molecular samples can help a person to visualize these useful three-dimensional relationships more clearly.

Depending on the semester and your individual class and laboratory sections, this laboratory may or may not precede the classroom discussion of the topic of *chirality* or handedness of molecules. After you explore this topic in class, perform this laboratory, and work with models on your own, the concepts will become clearer to you

Your instructor has probably noted that the properties of molecules that are enantiomers (non-superimposable, mirror-image molecules) are seen to be identical for all achiral measurements. There is, for example, nothing handed about melting points, density, and boiling points. Yet, when we observe enantiomers with chiral tools, such as the plane polarized light in a polarimeter, the inherent handiness can be seen.

Plane polarized light is formed from right and left handed circularly polarized light. Chiral molecules interact differently with the right and left handed components of plane polarized light producing an observed rotation, alpha (a), of the plane in which the polarized light is vibrating. In this laboratory, using a polarimeter, you will observe the ability of some chiral molecules to rotate a beam of plane polarized light. In addition, you will measure the specific rotation, [a], for some chiral molecules such as R- and S-carvone and R- and S-limonene.

Recall from the lecture or from the lecture text that specific rotation, [a], is related to the observed rotation, a, by the following formula:

Equation 1
$$[\alpha]_{D}^{T} = \frac{\alpha_{observed}}{l_{(decimeter)} \times c_{(g/mL)}}$$

In this expression, the specific rotation at a temperature, T, using sodium vapor light, D, equals the observed rotation, alpha, divided by the length of the sample tube in decimeters and the concentration of the sample in grams per mL. Recall that 10 centimeters equal one decimeter. In the case of a pure liquid sample, which has not been diluted with solvent, the concentration of the pure liquid is simply the density of the liquid (since density, itself, has the dimensions of g/mL). You will need to refer to one of the handbooks to find the density of the pure compounds that you examine. The temperature will be the ambient room temperature.

Reading and Pre-Lab Assignments

Read the sections in your textbook on enantiomers and optical activity before doing this laboratory.

In addition, perform a literature search on the following molecules. You will want to record their structure, density, and specific rotation in your notebook. A copy of a compilation of data from a variety of literature sources is appended to this lab.

(+) and (-) carvone (perhaps listed as *d or l*)

(+) and (-) limonene (perhaps listed as *d or l*)
sucrose

Before you come to the laboratory, do the Pre-Lab assignments for this laboratory as assigned by your instructor.

Prepare your laboratory notebook as required by your instructor.

Analysis using the Chemical Polarimeter

The Vernier Chemical Polarimeter uses an LED light source, a polarimeter fixed in place and one that rotates (generally referred to as an analyzer). The data is collected on a computer or handheld device. As the analyzer is rotated, the rotating light will be transmitted at varying angles, which can be seen by measuring the intensity of the light transmitted. Every sample will have characteristic peak and minimal angles, which can be used to determine properties of the sample.

Procedure when using a laptop

Log into the computer using your Stockton log-in. Open the software LoggerPro, located in the Course Applications folder. Connect the LabQuest mini into the computer and plug the polarimeter into it. The software should automatically recognize the polarimeter and display a graph with illumination along the y-axis and angle along the x-axis. Place the water sample into the polarimeter. In order to determine the angle of rotation for a sample, a reference sample must be used, comparable to taring a balance to define the zero point or zeroing spectrophotometer against a blank solution. Water is a suitable blank for this lab.

Place the water sample in the polarimeter. Start data collection and slowly rotate the analyzer clockwise or counterclockwise until collection stops. A slow rotation produces a smoother curve and thus higher quality data. Record the first angle above 0° where the angle is at a maximum for the blank. A more accurate measurement of this angle can be obtained by using a fitting curve. See the Vernier video for an explanation of how to do a curve fit. Store the run.

Now place your optically active sample in the polarimeter. Start data collection and slowly rotate the analyzer until data collection stops. Record the first angle above 0° where the illumination is at a maximum. The angle of rotation, α, is the difference between the measured angle of the sample and that of the blank: $\alpha = \text{Angle}_{sample} - \text{Angle}_{blank}$.

Measure the length of the sample to the nearest 0.1 cm and convert to decimeters. Use this data and the literature value for density to calculate the specific rotation, [a], of the sample.

Our Study Samples

The enantiomeric carvones make excellent study samples. Oil of Caraway contains one enantiomer while its mirror image is the principal component of Oil of Spearmint. Similarly, the enantiomeric limonenes can also be obtained from different plant sources.

(R)-(-)-Carvone   (S)-+)-Carvone   (S)-(-)-Limonene   (R)-(+)-Limonene
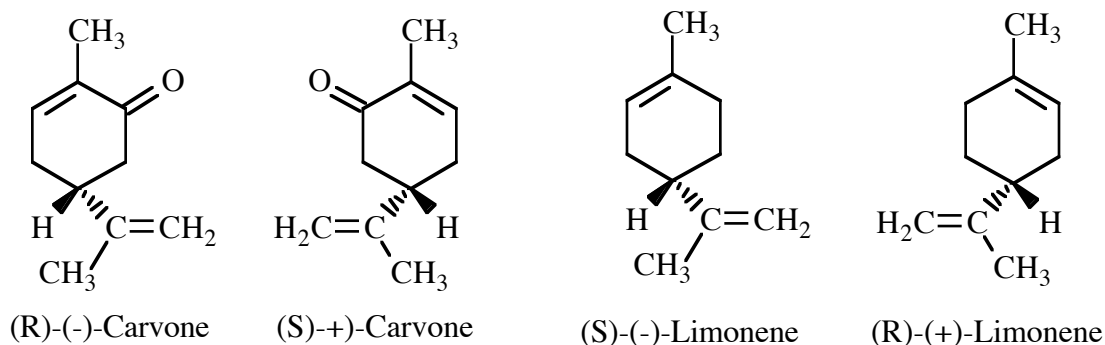
Experiments

We have prepared many of the samples for these experiments and have placed them in wooden support blocks. There should be one set of samples for each polarimeter. Your instructor will provide other chemicals and supplies.

A. Determine the Specific Rotation of R Carvone and R Limonene.

Your sample block will hold vials containing **neat** (this means there is no solvent), (R)-(-)-carvone and (R)-(+)-limonene. The specific rotations of these two samples are close to the best literature values of these substances, indicating that they are quite pure. Determine their specific rotations using the polarimeter. The tops or stoppers will have to be removed to see into the sample tube. Take great care not to switch tops and stoppers between sample tubes since the exchange of tops or stoppers will contaminate the samples and change the observed rotation. As noted above, each determination will consist of 1) measuring the observed rotation, 2) measuring the length of the sample in the tube, 3) finding the concentration by looking up the density in a handbook and 4) performing the calculation. Compare your experimentally determined specific rotations with the values in the Aldrich Catalog, the supplier of these samples. Your values should agree fairly well with these values. If they are off by more than 10%, perform the experiment again.

B. Determination of the Enantiomeric Excess in impure samples.

In the first experiment, our goal was to see how well our polarimeters work by comparing the values of specific rotation with those measured by the supplier of the samples.

This next experiment has a different goal. S-(-)-Limonene and S-(+)-carvone of high chemical purity can be obtained from a number of plant sources. Even though the samples are over 96% pure, our samples do not have nearly the same optical activity as the literature values for the pure enantiomers. This is because they are enantiomerically impure. They consist of a mixture of both enantiomers with an excess of one of them.

Consider a sample of 100 molecules. If 80 of these molecules had the R-configuration and 20 of these molecules had the S-configuration, the optical rotation of these molecules would be only 60% of the rotation of the pure R molecules. The rotation of the 20 S- molecules will exactly cancel out the rotation of 20 of the R-molecules, leaving 60 R-molecules to rotate the light. Such a sample would be said to have an *enantiomeric excess of 60%.* 60% of the mixture is pure R and 40% of the mixture is a *racemic mixture* (defined as a 1:1 mixture of enantiomers). Work this out in your own mind until you understand it. The mathematics is really very straightforward:

$$\% \text{ Enantiomeric excess } = \frac{\text{moles of one enantiomer - moles of other enantiomer}}{\text{total moles of both enantiomers}} \times 100$$

Equation 2

For our purposes, we can use the optical rotations to determine the same thing:

$$\% \text{ Enantiomeric excess (or ee) } = \frac{\text{observed specific rotation}}{\text{specific rotation of the pure enantiomer}} \times 100$$

Equation 3

Determine the **specific** rotation of the samples of (S)-(-)-limonene and (S)-(+)-carvone. Calculate their enantiomeric excess (ee) by comparing the **specific** rotation with the literature value obtained from the Merck Index. (You see, the "literature" value from the Aldrich Catalog is simply a report of the specific rotation of the enantiomerically impure sample we purchased.)

C. Identification of an Unknown Carvone or Limonene Sample

Your sample block should contain a tube with an unknown # on it. This will be a sample of one of the carvones or limonenes that has been prepared by dissolving some of the sample in ethanol. The concentration of the solution will be given. Determine the specific rotation of this sample and use this data to determine the identity of the unknown by comparison with the experimental values of the specific rotations you have determined.

D. Concentration of a Sucrose Solution.

Cane sugar, or sucrose, is an important commercial substance and its specific rotation is already known and listed in the handbooks. If you know that a solution has been made from sucrose, but you don't know the concentration of the sucrose, you can measure the observed rotation, a, and calculate the concentration of the sucrose using the specific rotation, [a], from a handbook.

One or more solutions may be assigned. The unknown solutions may be labeled A, B, C or some other designation.

Be sure that you understand that this last experiment is asking for a different kind of answer from all of the previous ones. You are NOT being asked to calculate the specific rotation of your sucrose solution! You cannot do this with the data you have. You are being asked to calculate the CONCENTRATION of the unknown sucrose solution. Equation 1 has four variables. You can

experimentally determine two of these. You can look up one of these. You can solve the equation for the missing concentration.

Summary
1. The mirror images of an optically active compound are called enantiomers.
2. When a light ray is made to oscillate on a single plane, it is said to be plane polarized.
3. An optically active compound will rotate the plane of polarization of plane polarized light.
4. For a compound to be optically active, it is necessary that it has no mirror plane of symmetry.
5. For a compound to be optically active, it should have one or more stereogenic centers (a carbon center attached to four different groups).
6. Know how to calculate the specific rotation of a compound.
7. Given the specific rotation and the observed rotation of a compound, along with the length of the polarimeter cell, you should be able to figure out the concentration of the sample.
8. Know what is meant by enantiomeric excess and how to calculate it.

Questions
1. Determine whether the following statements are true or false and provide the chemical basis for your answer.
   (a) The specific rotation of a compound is independent of any other parameters.
   (b) In general, density can be used as concentration for a pure liquid.
2. A solution of an unknown compound (3.0 g of the compound in 20.0 mL of solution), when placed in a polarimeter tube 2.0 dm long, was found to rotate the plane of polarized light $1.8°$ less than the water sample. What is the specific rotation of the compound?
3. The correct units for specific rotation are deg cm^2 g^{-1}, although the unit is usually just given as degrees. Can you show how the unit of specific rotation is deg cm^2 g^{-1}?
4. A carbon atom is said to be stereogenic if it is bonded to four different groups. Identify the stereogenic carbons in the following compound. Mark the stereogenic carbon(s) with an *.
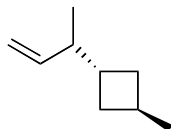
Literature Data for Polarimetry Laboratory

The following data comes from the 2000-2001 Catalog from Aldrich, the company from which we have purchased these chemicals. Note that the reported specific rotations are those of these particular chemicals and may not agree with the best literature values because of enantiomeric impurity.

435759 ALDRICH
(S)-(+)-Carvone
96%
Synonym: (+)-Carvone, (S)-5-Isopropenyl-2-methyl-2-cyclohexenone, p-Mentha-6,8-dien-2-one

124931 ALDRICH
(R)-(−)-Carvone
98%
Synonym: (−)-Carvone, (R)-5-Isopropenyl-2-methyl-2-cyclohexenone, p-Mentha-6,8-dien-2-one, Carvol

vapor density	5.2 (vs air)
vapor pressure	0.4 mmHg (20 °C)
assay	98%
optical activity	[α]20/D −61°, neat
optical purity	ee: 98% (GLC)
refractive index	n20/D 1.497(lit.)
bp	227-230 °C(lit.)
density	0.959 g/mL at 25 °C(lit.)

assay	96%
optical activity	[α]23/D +54°, neat
refractive index	n20/D 1.497(lit.)
bp	96-98 °C/10 mmHg(lit.)
density	0.96 g/mL at 25 °C(lit.)

218367 ALDRICH

(S)-(−)-Limonene
96%
Synonym: (−)-p-Mentha-1,8-diene, (−)-Carvene, (S)-4-Isopropenyl-1-methyl cyclohexene

183164 SIGMA

(R)-(+)-Limonene
97%
Synonym: (+)-p-Mentha-1,8-diene, (+)-Carvene, (R)-4-Isopropenyl-1-methyl-1-cyclohexene

vapor density	4.7 (vs air)
vapor pressure	<3 mmHg (14.4 °C)
assay	97%
optical purity	ee: 98% (GLC)
expl. lim.	6.1 %
refractive index	n20/D 1.473(lit.)
bp	176-177 °C(lit.)
density	0.842 g/mL at 20 °C(lit.)
Gene Information	human ... CYP1A2(1544)

vapor density	4.7 (vs air)
vapor pressure	<3 mmHg (14.4 °C)
	1 mmHg (20 °C)
assay	96%
optical activity	[α]19/D −94°, c = 10 in ethanol
expl. lim.	6.1 %
refractive index	n20/D 1.471(lit.)
bp	175-177 °C(lit.)
density	0.844 g/mL at 25 °C(lit.)

247618 ALDRICH

Sucrose
ACS reagent
Synonym: α-D-Glc-(1→2)-β-D-Fru, α-D-Glucopyranosyl β-D-fructofuranoside, β-D-Fructofuranosyl-α-D-glucopyranoside, D(+)-Saccharose, Sugar

grade	ACS reagent
optical activity	[α]25/D +66.3 to +66.8°, c = 26 in H$_2$O
impurities	≤0.0008 meq/g
	≤0.005% insolubles
	≤0.05% invert sugar
ign. residue	≤0.01%
loss	≤0.03% loss on drying
mp	185-187 °C(lit.)
anion traces	SO$_4^{2-}$ and SO$_3^{2-}$: ≤0.005%
	chloride (Cl⁻): ≤0.005%
cation traces	Fe: ≤5 ppm
	heavy metals: ≤5 ppm