Synthesis and Physical Properties of Liquid Crystals: An Interdisciplinary Experiment

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Introduction

Rationale for Experiment

Many exciting research questions lie at the intersection of the disciplines of chemistry, biology, and physics. Through a recent curricular innovation at Harvey Mudd College, we engage first-year students in an introductory laboratory course, the ID Lab, that illustrates the interdisciplinary nature of science today. In designing our ID Lab, we sought experiments that blend the fields of chemistry, biology, and physics and emphasize question and hypothesis formulation and testing *(1, 2)*.

This current experiment involving the synthesis and physical properties of liquid crystals beautifully illustrates the interdisciplinary nature of liquid crystal research and the practical devices derived from such research. While naturally occurring liquid crystalline materials are known and the first liquid crystals discovered were derivatives of cholesterol, the materials for practical use have been synthesized to provide the specific physical properties necessary for various display applications. This experiment introduces a synthesis component that complements the physical measurements to illustrate the interplay between desired physical properties and the often necessary requirement to make new materials to provide those properties. The physical property featured here is the pitch of a chiral nematic liquid crystal. This property is responsible for the colors seen in many applications of liquid crystals. The measurement of the pitch invokes the use of refractive index properties and the transmission of visible light through liquid crystalline samples. Mixtures of liquid crystalline materials allow work at convenient laboratory temperatures. Further the use of mixtures introduces the practical application of a binary phase diagram to find composition regions that provide convenient temperatures for laboratory measurements. Since cholesterol and its derivatives often play crucial roles in human physiology, understanding the properties of such materials adds an important biological character to the experiment.

Curricular Placement

The ID Lab is part of our required first-year curriculum in which all students take one year of general chemistry lecture and laboratory and one year of introductory physics lecture with a one-semester laboratory. Enrollment in ID Lab is limited to thirty-six students selected on the basis of their interest in the laboratory. The students enrolled in the ID Lab substitute this course for the fall chemistry laboratory and the spring physics laboratory. The ID Lab has been offered for the last six years beginning with academic year 1999–2000.

Operationally each experiment in ID Lab lasts three laboratory periods with the first two periods generally devoted to measurements and the third period devoted to data analysis and report writing. Prelaboratory assignments are posted on the course Web site and are due before the first and second laboratory periods. The "prelab" responses are submitted via email to the instructor and consist of calculations to illustrate those necessary in the laboratory.

Curricular Connections

This experiment involves multiple chemistry and physics concepts applied to a state of matter that has biological relevance. Aspects of Lewis acid–base principles are illustrated by the synthetic route employed to make one of the components in the mixtures studied. The concepts of refractive index and anisotropy in the optical properties of materials are introduced and employed when making the refractive index measurements. The notion that classes of liquids can organize and exhibit order while still fluid is introduced. How ordered fluids can form macroscopically from the building up of microscopic structures is illustrated by the determination of the pitch and the handedness of the supramolecular helix exhibited by a chiral nematic phase. The interaction of polarized light with matter and thus the introduction of properties of polarized light is illustrated by selective reflection measurements. While the basic properties of light are believed to be understood by students from their high school background, the experimental write up provides the background material to appreciate polarized light and the diffraction of light. We conduct this experiment in the second semester of the first year after students have acquired some of understanding of visible spectroscopy for the selective reflection measurements.

Liquid Crystals

A liquid crystal is a state of matter neither liquid nor crystal but a state in-between *(3)*. Liquid crystals are often called mesophases after the Greek *mesos* for middle. A crystal is a collection of molecules (or atoms) positioned and oriented in space in a regular, repeated manner. An ordinary liquid is a collection of molecules neither positioned nor oriented in any regular manner. Normally when a crystal melts it forms an ordinary liquid phase without order, that is, isotropic. However, a substance that exhibits liquid crystalline behavior "melts" at least twice, first into the liquid crystalline or mesophase, and second into the ordinary liquid. All molecules in a mesophase orient with respect to each other and, in certain types of liquid crystals, further exhibit some regular position with respect to each other. Thus, mesophases are described by degrees of orientational and positional order. Using ordering as a basis, liquid crystals fall into two types: nematic and smectic. A nematic mesophase possesses only orientation order while smectic mesophases possess orientational and some positional order.

Molecular views of the simpler mesophases—nematic, chiral nematic, and smectic A—are shown in Figure 1. The chiral nematic is a special type of nematic phase. In the chiral nematic phase the molecules comprising the phase more-or-less point in the same direction on a local scale; on a larger scale that pointing follows a helical pattern as illustrated in Figure 1. The quantity called pitch is also illustrated in Figure 1 and is the physical distance required for one complete revolution about the optical axis. The chiral nematic phase is often still called by its original name of the cholesteric phase. Today cholesteric liquid crystalline materials are recognized as nematic mesophases formed by optically active or chiral molecules and hence, chiral nematic is now considered the more descriptive name. The optical activity of the individual molecule imparts the macroscopic helical arrangement to the nematic phase. The name cholesteric comes from cholesterol benzoate, the first substance observed to exhibit what we today call liquid crystallinity. Many commercial liquid crystal devices employ the chlolesteric phase to function, making cholesteryl derivatives important objects of study. Curiously, cholesterol does not exhibit any liquid crystalline phases. The study of cholesterol derivatives gains further importance since such materials are components of the deposits that form on the wall of arteries leading to the hardening of the arteries.

A nematic mesophase forms when rodlike molecules orient themselves on average in a given direction. The director of the phase is a vector that points in a direction determined by looking at the average of the directions in which all the molecules point or are oriented. The director's orientation varies with temperature, pressure, applied electric and magnetic fields, and, for mixtures, composition. The many practical applications of liquid crystals depend critically on modifying the director by external influences. An important aspect of this experiment is the study of the factors that affect the director of the cholesteric phase, which is the direction in which any *local* collection of molecules points. What happens to the cholesteric director is studied by determining the pitch of the helix in the chiral nematic phase as a function of temperature and composition.

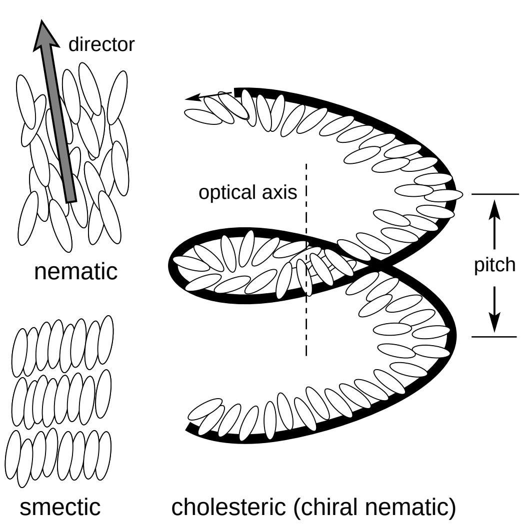

Figure 1. Schematic drawings of three mesophases: nematic, cholesteric (or chiral nematic), both of which only have orientational order, and smectic that has orientational and positional order. The smectic phase illustrated is properly known as a smectic A.

Substances in their liquid crystalline phase behave like liquids in that they flow and fill any shape container in which they are placed. However, though they are fluids, they retain certain optical properties characteristic of a solid, especially those optical properties that depend on polarized light. In the cholesteric mesophase the director follows a helical path (Figure 1). The sense of this helix, left or right, determines the sense of the angle of rotation of plane polarized light passing through a cholesteric sample. The pitch of the helix also depends on external influences. The pitch depends on temperature and pressure, and, for mixtures, also on composition.

Experimental

Chemicals

Commercially-available reagents were used as obtained: cholesterol chloride (Fluka or Aldrich), cholesteryl pelargonate (or cholesteryl nonanoate; Fluka), cholesterol (Fluka from lanolin), HPLC-grade pyridine (Aldrich), ACS-grade acetone (Aldrich). Sulfuric acid, 1 M, was made by dilution of the concentrated acid.

Equipment

Synthesis

Flasks, filtration equipment, magnetic stirrer hot plates, graduated cylinders, and disposable syringes for delivery of the acid chloride were the basic equipment required.

Refractive Indices

Abbe-type refractometers with circulating water baths to provide temperature control were used. Calibration was performed with solid test pieces to avoid temperature dependent calibrations.

Selective Reflection

Beckman DU650 spectrophotometers fitted with temperature-controllable sample holders were used. Circulating water baths provided temperature control. The temperature of the sample was measured with a digital thermocouple. An Omega Model HH21 or equivalent with a T- or K-type thermocouple proved adequate to the task. Plastic polaroid sheets, whose axis of polarization had been determined, were used to polarize the light for the selective reflection measurements. The quarter-wave plates used to determine the handedness of the helix were 3M circular polarizers of 10% neutral transmission cut for left-handed orientation and available from Edmund Scientific. Microscope slides, Mylar film, and cellophane tape are used to construct the sample "sandwich."

Procedures

Schedule

This experiment is constructed as follows. Week 1: synthesis of the cholesteryl nonanoate; preparation of mixtures of cholesteryl nonanoate and cholesteryl chloride; measurement of the refractive indices of mixtures as a function of temperature. Week 2: measurement of the selective reflection as a function of temperature; measurement of the handedness of the mixture studied. Week 3: analysis of the refractive index and selective reflection data to calculate pitch.

Synthesis and Characterization

Cholesteryl nonanoate (ChNon), an ester derivative of cholesterol (ChOH), is synthesized through an acid chloride–alcohol condensation. The synthesis reaction is conducted in dry pyridine using fresh reagents, especially the nonyl acid chloride (NonCl).

$$\text{ChOH} + \text{NonCl} \rightarrow \text{ChNon} + \text{HCl}$$

Quantities used are based on 1.5 g of cholesterol starting material. The typical time for the synthesis is approximately 1.5 hours. While the synthesis here focused on the acid–base condensation reaction, an additional synthesis could be added to the experiment by making the acid chloride from nonanoic acid and thionyl chloride. Such an experiment was described by Patch and Hope in this *Journal (4).*

The product is recrystallized from acetone and its two "melting points" checked to confirm the synthesis. Cholesteryl nonanoate forms a chiral nematic, that is, a cholesteric, liquid crystalline phase at 80 °C, which in turn melts into the isotropic, normal liquid phase at 93 °C .

Sample Preparations

While cholesteryl nonanoate is successfully synthesized by the students, commercially-available cholesteryl nonanoate and cholesteryl chloride are used to make the necessary mixtures to avoid issues of impurities. Cholesteryl nonanoate is mixed with cholesteryl chloride (ChCl), another chiral nematic whose cholesteric phase appears around 70 °C. Mixtures yield cholesteric (chiral nematic) phases at convenient temperatures, 45 to 65 °C, and compositions, 0.38 to 0.5 cholesteryl chloride mole fraction, x_{ChCl}. The masses necessary to make a desired mole-fraction mixture are weighed by difference, physically mixed, and then allowed to melt mix in a 70 °C oven for about 20 minutes. The class is divided into groups and each group further divided into teams of two students each. A group is responsible for working with a given mole-fraction mixture and a team is responsible for making refractive index measurements at specific temperatures on the group's assigned mole-fraction sample. The aim of this labor division is to reduce the number of measurements made by each team, thereby decreasing the experiment length, and providing the opportunity for the students to share their data to calculate the pitch of the mixtures as a function of temperature and ultimately note the effect of composition on pitch at fixed temperatures.

Refractive Indices

One mixture from each group was placed on the prism of an Abbe refractometer by spreading enough of the melted mixture to cover the bottom prism. The upper prism was then closed. The refractive index lamp and the dispersion correction are then adjusted to find two lines in the field of the refractometer *(5).* By rotation of the sheet of plastic linear polarizer held over the refractometer eyepiece, one or the other of the two lines in the field of view can be isolated, and the instrument adjusted to read the refractive index.[1] A sequence of field views is shown in Figure 2. The parallel index is greater than the perpendicular index. The teams made refractive index measurements at temperatures varied from 45 to 65 °C in increments of 5°. The time required for a group of three teams to make measurements at four to six temperatures would be on the order of two hours. These measurements were often made during the waiting time of the synthesis.

Selective Reflection

A plastic linear polarizer piece is placed in the light path of the sample chamber of the UV–vis spectrophotometer, taped to the side of the chamber over the opening where the light exits the monochromator. The liquid crystal sample is a sandwich made by spreading a small quantity, on the order of 0.05 mL, of the melted liquid crystal mixture on a microscope slide, with some Mylar tape as a spacer placed away from the sample at the ends of the slide. Another slide is then placed on top and the two slides taped together with cellophane tape. The placement of this slide sample in the spectrophotometer chamber depends on the design of the sample holder. In our case the Beckman DU650 allowed the slide to be placed flat against the cuvette holder in such a manner to pass light through the slide while the slide made good thermal contact with the thermostated cuvette holder. Temperature control was obtained by water circulating through the cuvette holder. Once in place, a transmission spectrum was recorded and the temperature then increased *(6).* Data at four or five temperatures in the range 40 to 70 °C were recorded. The measurement temperatures do not have to be the same as the temperatures of the refractive index measurements but should cover the same temperature range. The series of transmission spectra in Figure 3 illustrate the effect of temperature. Figure 3 is also typical student data. The minimum wavelength in the transmission spectrum determines the wavelength of maximum reflection that is called the selective wavelength. Since the minimum transmission occurs at different wavelengths at different temperatures, the wavelength of light reflected, that is the selective reflection, changes with temperature. The time required for this portion of the

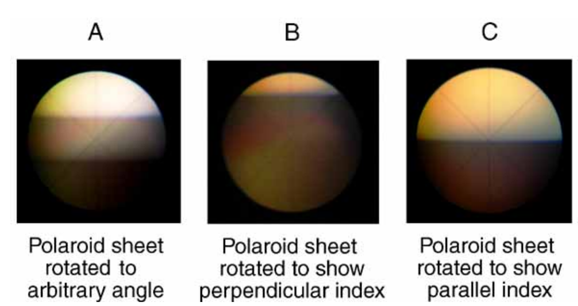

Figure 2. The refractometer field of view illustrating (A) the two refractive lines due to the parallel and perpendicular indices; (B) the field of view of the perpendicular index viewed through a linear plastic polarizer; and (C) the field of view of the parallel index viewed through a linear plastic polarizer. The perpendicular index is smaller than the parallel index. If in case (B) the instrument were adjusted to bring the light–dark line in correspondence with the crosshairs, an index value lower than that in case (C) would be read. The sample is a mixture of cholesteryl chloride and cholesteryl nonanoate.

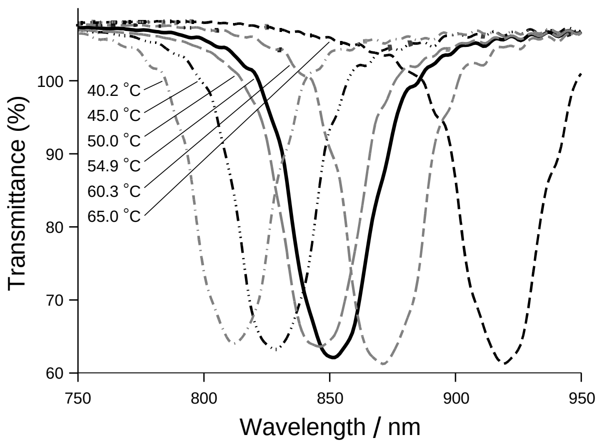

Figure 3. The wavelength at the minimum transmission is the selective reflection at the temperature of the spectrum. The sample is a 0.461 mole fraction cholesteryl chloride in cholesteryl nonanoate mixture. The minimum transmission moves to longer wavelength as temperature increases. The series above goes from λ_{min} (40.2 °C) ≈ 815 nm to λ_{min} (65.0 °C) ≈ 920 nm.

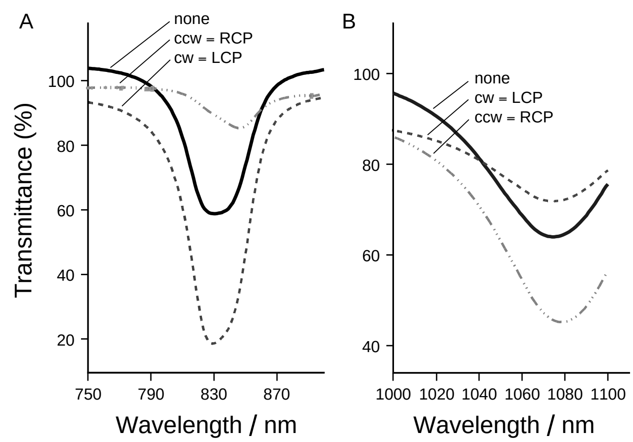

Figure 4. The transmission and reflection of left and right circularly polarized light at 45 °C: (A) by a sample of x_{ChCl} = 0.456 and (B) by a sample of x_{ChCl} = 0.801. Left circularly polarized (LCP) light is reflected by left-handed helices and transmitted by right-handed helices. Vice versa for right circularly polarized light (RCP). The quarter wave-plate used produces LCP when its optical axis is rotated clockwise 45° from the optical axis of the linear polarizer. For a spectrum labeled cw, the incident light is left circularly polarized and right circularly polarized for a spectrum labeled ccw.

experiment greatly depends on the speed with which the temperature of the sample can be changed in the spectrophotometer chamber. We have typically allotted the second laboratory period for these measurements.

Handedness

The test for the handedness of the helix of the chiral nematic should be made for at least one temperature *(6, 7).* By inserting a quarter-wave plate in the light path after the linear polarizer but before the sample, circularly polarized light is produced and is incident on the sample. The supramolecular organization of the chiral nematic molecules interacts with circularly polarized light. If the helix is left-handed, then right-handed circularly polarized light passes through the sample, and the transmission spectrum should show no minimum indicative of reflection. For a left-handed helix, left-handed circularly polarized light is reflected. In other words when the left circularly polarized sheet is placed in the light path rotated 45° counterclockwise from the axis of the linear polarizer, the transmission spectrum should show a minimum when the helix is left-handed. Rotating the quarter-wave plate 90° clockwise from its initial orientation should give a transmission spectrum without a minimum, showing that now the right-handed circularly polarized light passes without reflection through the left-handed helical structure of the chiral nematic phase. In this study at 45 °C the helix is left-handed below 0.6 mole fraction of ChCl and right-handed above 0.6. This assignment of handedness is confirmed in Figure 4; Figure 4A illustrates that left circularly polarized light is selectively reflected and right circularly polarized light transmitted for the sample whose composition is mole fraction cholesteryl chloride 0.458, which means the handedness of the sample is left. For the mole fraction 0.801 sample (Figure 4B), the opposite behavior implies that the handedness of the mixture is right.

Hazards

The synthesis is best done in a fume hood or under a flexible fume duct commonly available in newer laboratory designs. The syntheses described here were conducted under such ducts. The acid chloride is a lachrymator and corrosive. The students wear protective gloves when conducting the reaction and recrystallization procedures. Waste materials are disposed of in suitably marked containers available in fume hoods. The mixtures as solids or liquid crystals pose no immediate skin or inhalation hazards.

Sample Student Results for Pitch

Sample refractive index data as a function of temperature for a fixed x_{ChCl} are presented in Figure 5. The average refractive index, n_{ave}, is calculated from the individual parallel, n_{para}, and perpendicular, n_{perp}, refractive indices by

$$n_{ave} = \frac{n_{para} + 2n_{perp}}{3}$$

This expression can be understood by the observation that the liquid crystals dealt with here are viewed as uniaxially birefringent, which means two of the general three refractive indices are equal to each other (perpendicular) and less than the third index (parallel). Uncertainty ranges for the data points were calculated by the propagation of error addition in quadrature method. These uncertainties were found to be small compared to the size of the data markers when plotted.

Figure 6 presents the dependence of selective reflection on temperature for a two compositions (upper two lines) and pitch as a function of temperature for the same two compositions (lower two lines). The pitch results are for left-handed

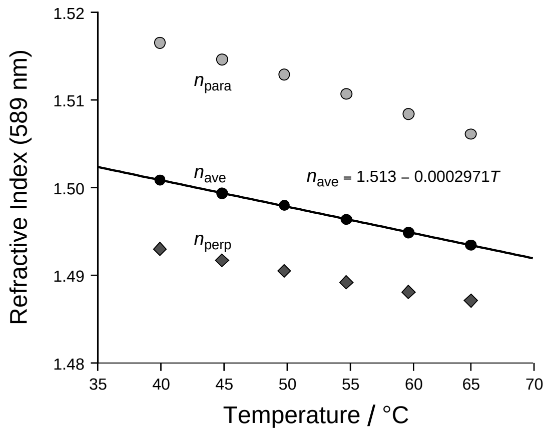

Figure 5. The measured parallel and perpendicular refractive indices with the calculated average refractive index as functions of temperature (T) for for x_{ChCl} = 0.461. These are sample student data that match theory well.

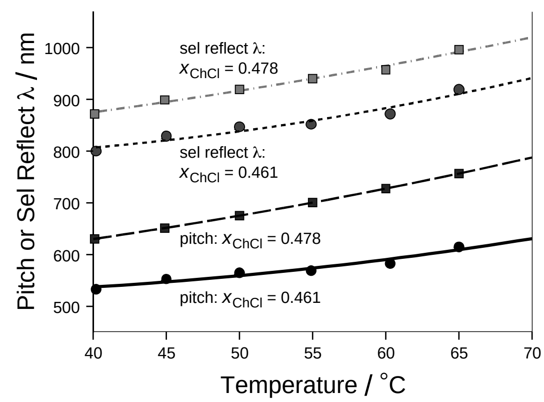

Figure 6. Selective reflection and pitch as functions of temperature for the two values of x_{ChCl}: 0.461 and 0.478.

chiral nematic mixtures. Uncertainty ranges in the plotted data are estimated in the measurement of the selective reflection peak maxima and found to be small compared to the size of the data markers. The selective reflection line is a simple second-order polynomial fit. The pitch of the chiral nematic helix is calculated from the quotient of the selective reflection wavelength and the average refractive index, each at the same temperature. To "obtain" these data at the same temperature, the average refractive index is fit to a straight line function of temperature and the selective reflection is fit to a quadratic in temperature. Then the pitch can be calculated as a function of temperature by evaluating the ratio of the two fitted lines at any temperature desired.

Assessment

The students were surveyed on aspects of the laboratory, and the interdisciplinary nature of the experiment was definitely recognized by the students. Their responses to the question "How was this experiment interdisciplinary?" are interesting (List 1). Students seem to confuse what might be considered the traditional areas of biology, chemistry, and physics, perhaps because the experiment has successfully reduced discipline-specific pigeonholes for knowledge. Clearly students recognized the use of physical techniques to study chemical structures, even when the structures were the supramolecular organizations exhibited by liquid crystalline phases. Assessing other aspects of the laboratory on a scale of 1 (not improved) to 5 (greatly improved), students felt that the experiment significantly enhanced their skills in analyzing and interpreting data (3.7), strongly improved their ability to collect and record scientific data (3.5) and to formulate and test a scientific question (2.8), promoted their ability to work with a partner (3.4), and strongly enhanced their skills to communicate scientific results to others (3.6). The survey size consisted of the thirty-six class members.

Some aspects of the experiment the students enjoyed the most were: working with liquid crystals (42%) and observing the phase transitions (19%). Aspects enjoyed least by the students were: waiting for the spectrophotometers to reach temperature (32%) and finding by trial and error a suitable quantity of liquid crystal to use for the spectral sample (16%). The most common suggestion for improvement called for improved temperature control, actually the rate of reaching temperature control, in the spectrophotometer cell holder.

List 1. Responses to the Question "How Was the Experiment Interdisciplinary?"

Number of Similar Responses	Student Responses (n = 36)
10	Biology of crystals, chemistry that causes solidification, liquidification, etc.
8	Chemistry—the synthesis and creation of liquid crystals through a chemical process with basic products; physics—analyzed the retention of light through the liquid crystals and related it to temperature.
5	Chemistry in the mixing and formulating of the liquid crystals. Physics was related to the formulations and changes of the crystals.
3	The chemical properties of a substance can influence its optical properties, and how optics can be used to determine chemical structure.
2	Crystal chemistry and refraction.
2	Liquid crystals—chemistry, spectroscopy involved physics.
2	Chemistry and physics.

Curricular Successes of the Experiment

The combination of seemingly different experiments—synthesis, refractive index, and spectrophotometry—to lead to conclusions about the microscopic world of molecular liquid crystal organization is a symbiosis both fascinating and amazing to students. Error propagation calculations have proven highly successful at helping students appreciate how the uncertainties in their various measurements on different instruments combine to provide final realistic uncertainties in the calculated pitch. During the write up time, conducted in the third regularly scheduled laboratory period, student teams post their pitch-versus-temperature data for their assigned composition on a blackboard for discussion. Each team gives a brief oral report on their individual team results. Students are then asked to provide explanations for the temperature dependence of the pitch and the composition dependence of the pitch. Interesting discussion ensues when the class is asked to explain why pitch increases with temperature and increases with increasing x_{ChCl}. The composition dependence implies that the pitch of the helix formed by the smaller cholesteryl chloride molecules is actually larger than the pitch formed by the larger cholesteryl nonanoate molecules. Explaining the observed temperature and composition dependence of the pitch on a molecular basis proved to be an enjoyable challenge for the students.

Acknowledgments

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[W]Supplemental Material

The complete student experimental procedures, prelaboratory assignments with solutions, a MathCad worksheet for the pitch calculations, a sample grading sheet, and extra instructor's notes are available in *JCE Online.*

Note

1. A convenient way to prepare this eyepiece polarizer is to drill a 0.5-in. hole in the bottom of a plastic 35-mm film canister and glue a piece of plastic polarizer over the hole. The film canister will fit nicely over the Abbe's eyepiece.

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