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Introduction

In 1897, F.S. Kipping and W.J. Pope discovered that sodium chlorate and sodium bromate, although achiral in solution, are chiral in their crystalline forms.1 Currently, optically active crystals are being researched heavily due to their interesting properties and potential efficacy in optical devices.2 Today technological devices, such as laptop computer screens, increasingly require the use of crystal arrays. Another such device would be any instrument that employs optical principles in order to measure some unknown parameter. The pathlength through which light must travel in these optical devices is a crucial factor in regards to certain abilities of the instrumentation.3 Some instruments may require a variety of pathlengths, and thus require a special means by which to evaluate pathlength; or the position in which the crystal must be mounted could make it difficult to determine the pathlength by traditional means, such as using a micrometer. Another reason for devising an alternative method for determining pathlength is so that the pathlength could be monitored during natural crystal growth without disturbing the nucleation process.

In this experiment, it will be shown that the linear relationship between pathlength and observed rotation can be applied to predict the pathlength based on the observed rotation. It should be noted, however, that the method devised will only work for chiral crystals. When aqueous NaClO3 solution evaporates two rotamers will form that will rotate plane-polarized light in equal but opposite directions. Hence, the crystals must be separated to obtain linear correlations in regards to the two rotamers.

Background

A beam of light consists of magnetic and electric fields oscillating orthogonal to one another. In light, the electrical field oscillates in all possible planes orthogonal to the direction of motion. When the light passes through a plane polarizer, the electric field in the light that emerges oscillates in the plane parallel to the direction

of the polarizer.4 When this plane-polarized light is then passed through a chiral NaClO3 crystal, the plane of polarization is rotated either clockwise, or counterclockwise, thus denoting the crystals either "positive rotamers" or "negative rotamers."5 The angle through which the plane of polarization is rotated is termed the observed rotation and may be measured with a polarimeter.5

Theory

The pathlength of the crystal can be determined by utilizing the following equation,

$$l = \frac{\alpha}{[\alpha] \cdot c} \qquad (1)^6$$

where l denotes pathlength, α denotes the observed rotation, $[\alpha]$ denotes the specific rotation, which depends on the material, the temperature, and wavelength of the light source, and c denotes the concentration.

In this experiment, the chiral agent is the NaClO3 crystal, which is a solid, thereby having an activity coefficient of 1.7. Therefore, the concentration in this experiment is constant and need not be considered. Thus, by measuring the observed rotation and pathlength, a linear correlation may be found and later utilized to measure pathlength based on observed rotation.

Experimental

A 3.0-M solution of NaClO3 was prepared - vacuum filtered, poured into petri dishes and allowed to evaporate until solid crystals were visible. Because most of the crystals formed in a pyramid shape, the crystals were sanded until flat to allow for adequate stacking. The sanding of the crystals was accomplished by using jeweler's rouge which is used to finely polish crystals. The jeweler's rouge was put on a flat surface and toluene was added to it until it was a creamy texture. The crystal was then rubbed on the jeweler's rouge. The rouge had enough grit that the crystals were polished down close to flat. The thickness of each crystal was then determined using a digital micrometer. Then, using a polarimeter, (employing the D-line of a Na lamp source; α = 589.6 nm) the

Right-Handed Crystals		Left-Handed Crystals	
Pathlength (mm)	Observed Rotation (degrees)	Pathlength (mm)	Observed Rotation (degrees)
0.550 ± 0.022	1.50 ± 0.15	0.67 ± 0.07	1.45 ± 0.07
0.56 ± 0.04	1.60 ± 0.10	0.79 ± 0.07	2.00 ± 0.11
0.621 ± 0.029	1.46 ± 0.08	0.866 ± 0.009	2.24 ± 0.29
0.830 ± 0.027	2.30 ± 0.13	1.13 ± 0.03	2.89 ± 0.19
1.040 ± 0.021	2.33 ± 0.15	1.22 ± 0.09	2.46 ± 0.18
1.05 ± 0.03	2.80 ± 0.10	1.27 ± 0.05	3.14 ± 0.05
-----	-----	1.94 ± 0.10	5.38 ± 0.24
-----	-----	2.60 ± 0.06	8.4 ± 0.3

Table 1. Experimental data collected.

	Right-Handed	Left-Handed
R value	0.94	0.99
Standard Error	0.211	0.417
Linear Equation	$y = 2.25x + 0.26$	$y = 3.48x - 1.07$

Table 2. Regression analysis obtained in Microsoft Excel.

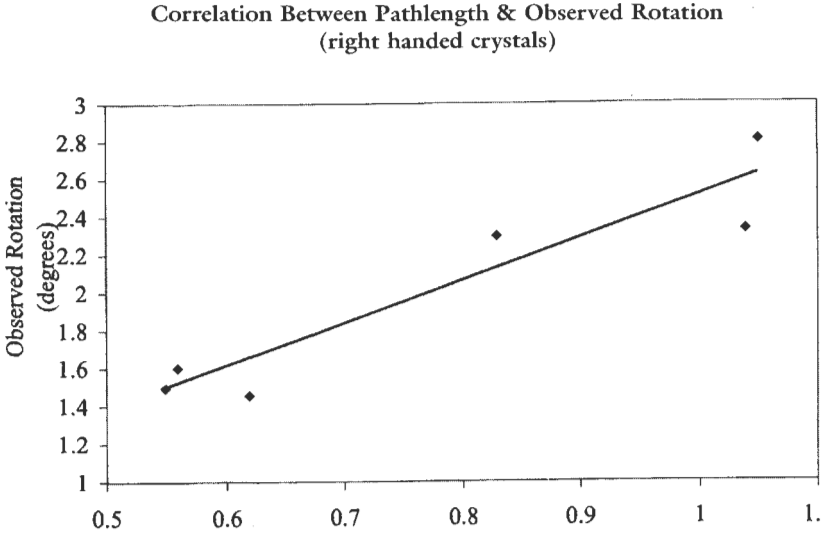

Figure 1

observed rotation of individual crystals, as well as some stacked crystals, was measured. All the measurements obtained were made nine times. The measured mean value and standard deviation of both parameters is outlined in Table 1. The results of the regression analysis are shown in Table 2.

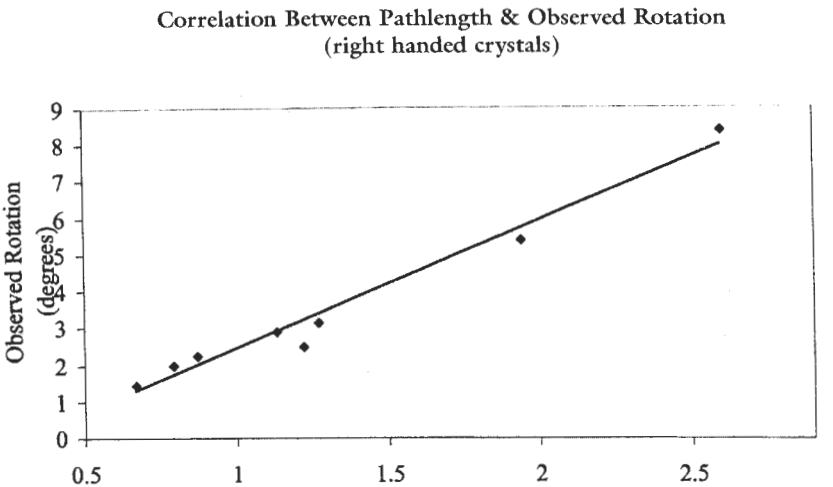

Figure 2

Conclusion

It can be seen that a linear relationship was observed, however, the data obtained is unsatisfactory for developing an accurate method for measuring crystal pathlength by observed rotation at this time. The reason for deviation from this line is thought to be due to the crystals not being exactly flat. Since they were not perfectly flat, the pathlength measurements taken with the digital micrometer were not very precise. In addition, the crystals must be flush to one another when stacked together in order to obtain accurate pathlength, which cannot be accomplished if the crystals are not perfectly flat. Through development of better sanding techniques, it is likely that this obstacle may be overcome. Future

experiments are also likely to entail utilizing a digital polarimeter and obtaining several hundred data points in order to obtain a more accurate and precise linear correlation.

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