Development of a Method for Measuring Magneto-Optical Rotatory Dispersion

Donald K. Loving
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DEVELOPMENT OF A METHOD FOR MEASURING MAGNETO-OPTICAL ROTATORY DISPERSION

by

Donald K. Loving

A Thesis
Submitted to the
Faculty of the School of Graduate Studies in partial fulfillment of the
Degree of Master of Arts

Western Michigan University
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Donald K. Loving
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CHAPTER I

INTRODUCTION

Historical

On 30 August, 1845, Michael Faraday set up an experiment which was almost identical to one which he had performed in September, 1822. The purpose of the experiment was to look for an effect that would demonstrate a relationship between light and an electric field. The experiment, which consisted of shining polarized light through a glass trough in which electrolytes were being decomposed, was, as the previous one had been, a failure. After numerous unsuccessful attempts, Faraday turned, on 13 September, 1845, to a series of similar experiments with magnetic fields and polarized light.

It was arranged so that light which was polarized by reflection from a plate of glass was analyzed by a Nicol prism. The prism could be rotated about an axis parallel with the direction of the light beam. Between the mirror and the prism and on the optic axis a plate, two inches thick, of lead borate glass was placed. This glass had a high refractive index. Poles of two electromagnets were oriented in various positions relative to the plate of lead borate glass. Pulsating, as well as constant, direct current was supplied to the magnets. The results of the experiment were recorded in Faraday's diary: 1
"It gave no effect when the same magnetic poles were on opposite sides (as respects the course of the polarized ray)—nor when the same poles were on the same side either with the constant or intermitting current—BUT when contrary magnetic poles were on the same side there was an effect produced on the polarized ray, and thus magnetic force and light were proved to have relation to each other."

The results of Faraday's further research on this effect were published in the Nineteenth Series of his "Experimental Researches in Electricity." The effect which he had observed had been the rotation of the plane of polarization of the polarized light. He drew three conclusions concerning the effect.  

1. The amount of rotation was proportional to the length of the light path through the material in the field.  
2. The amount of rotation was proportional to the intensity of the magnetic field.  
3. The sense of rotation was determined by the direction of the magnetic field relative to the direction of the light path.  

Although the Faraday effect was, in a sense, an induced optical rotation, the third of Faraday's findings meant that it had the important difference from natural optical rotation that upon reflection of the light back through the sample, the effect would be doubled rather than canceled.  

Verdet published the results of his investigations of the Faraday effect in four papers which appeared in Annales de Chimie et de Physique between 1854 and 1863. The first paper is summarized in Verdet's Law,  

\[ \chi = \text{VdHcos} \, r \]
ARRANGEMENT FOR OBSERVING THE FARADAY EFFECT

Figure 1
in which $\phi$ is the amount of rotation, $d$ is the path length through
the material, $H$ is the magnetic field strength, $r$ is the angle that
the incident light makes with the field direction, and $V$ is the
proportionality constant that bears his name. Verdet established
the convention of calling rotation in the same direction as the
current producing the magnetic field "positive." In his fourth
paper he disproved Wiedemann's Law that the magneto-optical rotation
was proportional to the natural optical rotation at the same
wavelength.\(^5\)

The explanations of the Faraday effect that have been put forth
are usually based on Fresnel's explanation of natural optical
rotation.\(^6\) Righi\(^7\) and Becquerel,\(^8\) working independently, showed
that the refractive index for right circularly polarized light
traversing a block of glass in the presence of a magnetic field was
different from that of left circularly polarized light. Brace\(^9\)
demonstrated that linearly polarized light decomposed in a magnetic
field into left and right circularly polarized beams. Since the two
beams travel through the material in the field at different veloc-
ities, they combine, upon leaving the field, to form a single beam
of linearly polarized light with a plane of polarization that has
been rotated from that of the incident beam.

Theoretical

For light shining through a substance the magnetic force on the
electrons can be neglected. However, if the material is placed in
an external magnetic field, $\mathbf{B}$, the force on the electrons is given by the Lorentz force expression

$$\mathbf{F} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}),$$

so that by treating the electrons as comprising an electron fluid the equation of motion becomes

$$\frac{\mathbf{s}}{m} + \mathbf{f} = -(\mathbf{E} + \mathbf{s} \times \mathbf{B}).$$

Choose the direction of $\mathbf{B}$ to be the positive $z$ direction, and assume that light is propagated in this direction. Let $\omega_0^2 = \frac{f}{m}$, and separate the components to obtain

$$\ddot{s}_x + \frac{e}{m} \mathbf{B} \dot{s}_y + \omega_0^2 s_x = -\frac{e}{m} E_x$$

$$\ddot{s}_y - \frac{e}{m} \mathbf{B} \dot{s}_x + \omega_0^2 s_y = -\frac{e}{m} E_y.$$  

Multiply the second of these equations by $\pm i$ and add the two to obtain

$$\ddot{s} + \frac{e}{m} i \mathbf{B} \dot{s} + \omega_0^2 s = -\frac{e}{m} E$$

where the following abbreviations have been used

$$s = s_x \pm is_y, \quad E = E_x \pm i E_y.$$  

The physical implication of using $E_+ = E_x + i E_y$ and $E_- = E_x - i E_y$ as the basic field variables is a transition from linear to circularly polarized light. For a monochromatic, plane polarized wave

$$E_x = A \cos(kz - \omega t), \quad E_y = 0.$$  

For the circularly polarized wave

$$E_0 = A \exp(i(kz - \omega t)).$$  

By applying the wave equation for conducting media one obtains, after simplification
Thus \( k_+ \) is not equal to \( k_- \).

Let the path of light in the magnetic field extend from \( z = 0 \) to \( z = d \). At \( z = 0 \)

\[
E_x = A \cos \omega t, \quad E_y = 0.
\]

To determine the values of \( E_\pm \) at \( z = d \), resolve \( k_\pm \) into two terms which are symmetric and antisymmetric, respectively, with respect to an interchange of \( k_+ \) and \( k_- \)

\[
k_\pm = \frac{1}{2}(k_+ + k_-) \pm \frac{i}{2}(k_+ - k_-).
\]

Then at \( z = d \)

\[
E_\pm = A \exp(i(\frac{d}{2}(k_+ - k_-) \pm \frac{d}{2}(k_+ - k_-) - \omega t)).
\]

Now by introducing the abbreviations

\[
\phi = \frac{d}{2}(k_+ + k_-) - \omega t, \quad X = \frac{d}{2}(k_+ - k_-)
\]

one obtains

\[
E_+ = A e^{i\phi} e^{iX}, \quad E_- = A e^{i\phi} e^{-iX}
\]

from which it follows that

\[
E_x = A e^{i\phi} \cos X, \quad E_y = A e^{i\phi} \sin X.
\]

This represents a linear oscillation which is rotated in a positive sense (right-handed screw direction around the magnetic field, \( \mathbf{B} \)) by an angle \( X \) with respect to the incident oscillation. \(^{10}\)

This derivation follows the one given by Sommerfeld. \(^{10}\) By using the expression above for \( k_\pm^2 \) and Verdet's Law he obtains an expression for the dependence of Verdet's constant on the frequency

\[
V = \frac{Ne^3}{2\pi m^2 c} \frac{\mu}{\varepsilon_0} \frac{\omega^2}{(\omega_0^2 - \omega^2)^2}.
\]
Expressing this in terms of wavelength one obtains the following expression for the amount of rotation, $X$:

$$X = K \frac{\lambda^2}{(\lambda^2 - \lambda_0^2)^2},$$

where $K$ is a constant. Since the wavelength $\lambda_0$ is assumed to be in the far ultraviolet, the dependence of the amount of rotation on the wavelength is approximately an inverse square relationship in the visible range of the spectrum.
CHAPTER II

THE EQUIPMENT

Figure 2 shows a sketch (not drawn to scale) of the equipment used to study the Faraday effect.

The Sources

The sources that were available were

1. a sodium arc source
2. a mercury arc source
3. a tungsten light bulb
4. a controlled spark source
5. a xenon arc source.

The sodium arc was used in measuring the strength of the magnetic field. The mercury arc had too few lines to be of use in taking rotatory dispersion measurements. The tungsten bulb was very useful for alignment of the optical path through the equipment. The controlled spark source had been previously constructed for use in studying the Faraday effect. When used with iron electrodes, it provided a great number of intense lines in the ultraviolet range of the spectrum. However, this source was less stable than the xenon arc, and source stability was an important factor in obtaining good results, as shall be explained in the next chapter. The xenon arc was a model 614 high intensity xenon arc purchased from O. C. Rudolph and Sons, Inc. Its spectrum is continuous in the range from
ARRANGEMENT OF EQUIPMENT USED IN STUDYING THE FARADAY EFFECT

Source  Polarizer  Electromagnet  Analyzer  Spectrograph

P = Pole Pieces
S = Sample Cell

Figure 2
200 to 700 μm. The xenon arc is very intense in the visible range of the spectrum, but it shows a 200-fold decrease in intensity at 250 μm relative to that at 400 μm. The light emerging from the xenon arc is focused, by means of a mirror behind the arc, to produce an image of the arc approximately 10 cm in front of the opening. An aluminum plate with a drill size 20 hole was taped to the front of the source to spacially limit this diverging beam.

The Polarimeter

The polarimeter, a model 80 high precision polarimeter, had been purchased from O. C. Rudolph and Sons, Inc. The polarizer was a split quartz prism, and the analyzer was a retarder (retarders are used in conjunction with linear polarizers in the production of circularly and elliptically polarized light and in the analysis of linearly polarized light13). Although the analyzer scale was calibrated to 0.001 degree of arc, the method which will be described in the next chapter did not permit full utilization of this precision.

The Magnet

The magnet had previously been constructed for use in research on the Faraday effect that had been conducted at The Upjohn Company.14 It was constructed with two wire compartments, each of which was wound with 1625 turns of number 13, round, lacquer-covered wire. In order to prevent burnout of the magnet during
Figure 3

On the table at the left is the power supply and cooling fan for the source. The flexible tubing carries air from the fan to the base of the housing for the arc.
operation, it contained three helical "pancakes" of copper tubing which were positioned between the wire compartments and at the ends of the magnet. During operation of an experiment tap water was run continuously through the tubing. This not only served to keep the wire temperature between 50 and 70 degrees Celsius, but it also maintained the sample at a temperature of approximately 17 degrees Celsius. Currents of from five to seven amperes at 110 to 140 volts were supplied to the magnet giving fields of from 2500 to 5200 gauss.

Sample cells were available which provided path lengths of 1 mm, 1 cm, 5 cm, and 10 cm (see Figure 4). The cells were purchased from O. C. Rudolph and Sons, Inc. and were supplied with parallel end plates of glass and quartz. The magnet was provided with two sets of pole pieces (see Figure 5) which were used to intensify the field in the sample. The cells were placed in the magnet between the pole pieces. One set of pole pieces was designed for use with the 10 cm cell, while the other set was for use with the smaller cells. The 1 cm and 1 mm cells both had about the same overall length, which was shorter than the length of the 5 cm cell. Therefore, steel slugs were inserted in the magnet core when the 1 cm cell and the 1 mm cell were used. These inserts effectively lengthened the pole pieces enabling higher field strengths to be obtained in the two smaller cells.

Field strength measurements were made by using the value for the Verdet constant for carbon disulfide taken from the Handbook of Chemistry and Physics. A sample of carbon disulfide was placed
Visible at the top from left to right are the 1 cm, the 1 mm, and the 10 cm cells (the 10 cm cell is only partially visible). At the bottom are the end plates for the three smallest cells and the 5 cm cell.
The set of pole pieces on the left is for the 10 cm cell. The set on the right is for the three smallest cells. The steel slugs are in the center.
in the magnet and measurements of the rotation of the plane of polarization at the 589.3 μ wavelength of the sodium arc were taken for several values of current to the magnet. The average value of the field strength in the sample at each value of the current was then calculated by means of Verdet's Law. The maximum field obtainable with the 5 cm cell was approximately 4000 gauss, while that with the 1 cm cell (when the steel slugs were used) was about 5100 gauss. Figures 6 and 7 show the curves for average magnetic field intensity vs magnet current for the 5 cm cell and the 1 cm cell (with slugs), respectively.

The Spectrograph

The spectrograph was a Hilger medium quartz spectrograph model E 498. Light entering through the adjustable slit at the front of this instrument was made parallel by a quartz lens. The light was then dispersed by a quartz Cornu prism and focused by means of a second quartz lens onto a photographic plate which recorded the resulting spectrum. Three types of plates were tried. Kodak SA3 plates were found to be the most useful, but Kodak SA1 and Kodak SWR (Short Wave Radiation) plates were also investigated.

The SA3 plates have a range from about 200 to 550 μ, while the range of SA1 plates is from about 220 to 480 μ. The SA1 plates provide higher contrast than the SA3 plates, but the latter are about three times as fast. Since the normal exposure times with the SA3 plates were from one to three minutes, with some exposures as...
FIELD INTENSITY VS CURRENT FOR THE 5 CM CELL

Figure 6

FIELD INTENSITY VS CURRENT FOR THE 1 CM CELL (WHEN USED WITH SLUGS)

Figure 7
long as ten minutes, and since from fifteen to twenty spectra were recorded on each plate, these plates were preferred to the slower SA1 plates. It was found that developing the SA3 plates in Diafine, a developer manufactured by the Baumann Photo-Chemical Corporation, gave increased sensitivity over the entire range of the plate and also increased the contrast obtainable with the conventional development materials.

An attempt was made to increase the sensitivity in the ultraviolet spectral range. A thin coating of fluorescent oil was spread on the SA3 plates before exposure and washed off with cyclohexane before development. This improved ultraviolet sensitivity, but it proved to be detrimental, not only to the plate holders, but also to the quality of the photographs. No accurate measurements could be obtained from these plates. An ultraviolet sensitizer, which was obtained from the Eastman Kodak Company, was prepared by dissolving it in cyclohexane. This solution, which when put on the plates formed a solid coating, did not damage the plate holders. However, the quality of the photographs was not good enough to permit accurate measurements to be taken.

The SWR plates have more sensitivity in the ultraviolet than either the SA1 or SA3 plates. This increased sensitivity is achieved by using a very thin emulsion. This thin emulsion was so vulnerable to damage from scratching that even with extreme care it was found impossible to obtain plates from which accurate readings could be taken.
Placement of the Equipment

Figure 8 shows the placement of the equipment used. The distance from the source to the polarizer was about 19 cm, and the distance from the analyzer to the spectrograph slit was about 15 cm.

The Microphotometer

After the plates were developed and dried, measurements were taken of the blackening of the plate on a Dietert type microphotometer, model 2255, which had been purchased from Applied Research Laboratories. This instrument gave a reading between 0.0 (no light transmitted through the plate) and 100.0 (clear plate). To obtain values for plate blackening, by which a higher number represents more light incident on the plate, the microphotometer readings would have to be subtracted from 100.0.
EQUIPMENT PLACEMENT

Figure 8
CHAPTER III

THE METHOD

As shown in chapter 1, the Verdet constant for a given substance is a function of wavelength. This means that if the values of the magneto-optical rotation at each wavelength of the spectrum are plotted vs wavelength, the result would be a curve which would be called a magneto-optical rotatory dispersion curve.

The Law of Malus states that the intensity of an analyzed beam of polarized light varies directly as the square of the cosine of the angle between the planes of the polarized and analyzed beams. Expressing this law as an equation, one obtains

\[ \frac{I}{I_0} = \cos^2 \theta \]

where \( I \) is the intensity of the analyzed beam, \( I_0 \) is the intensity of the incident light, and \( \theta \) is the angle between the planes of the polarized and analyzed light. The blackening of a photographic plate placed in the analyzed beam would be proportional to \( \log \frac{I}{I_0} \). Thus the blackening would be proportional to \( \log \cos \theta \). Figure 9 shows two plots of \( \log \cos \theta \) vs microphotometer reading. The data were taken from a plate exposed by shining light from a mercury arc source through 1 cm benzene. Two sets of spectra were photographed, each set consisting of spectra taken with varying analyzer positions. One set was taken with a field of approximately 2900 gauss.
Figure 9
in the sample, and the other set was taken with no field in the sample. The microphotometer readings were taken from the 326.4 mp line of the mercury arc spectrum. If one draws vertical lines which intercept both of the lines in Figure 9, and subtracts the values for the angles represented by these intercepts, one finds that the result is an angle of about 6° 18' at each value of blackening. Although the mercury arc source has far too few lines in its spectrum to be useful in obtaining magneto-optical rotatory dispersion curves by this means, the controlled spark source with iron electrodes would provide both enough lines and also sufficient intensity to make it practical. However, since this method would require from ten to twenty microphotometer readings at each spectral line for which the value of the rotation at that wavelength was desired, another, shorter method was sought.

The data in Figure 9 demonstrate that the Law of Malus is valid even when the angle that the polarized beam makes with the plane of the analyzer is not the same as the angle that the polarizer itself makes with the analyzer. When the light passed through the benzene in the magnetic field its plane of polarization was rotated. If light were passed through the benzene sample without the magnetic field, but with the polarizer set at the same angle to the analyzer that the rotated beam had made with the analyzer, a photographic plate placed in the analyzed beam would have received the same degree of blackening as one placed in the analyzed beam of the ro-
tated light. On the strength of this fact a modification of the graphical method was developed which required only three measurements at each wavelength where the amount of rotation was desired. Due to its greater stability, the xenon arc source was chosen over the iron electrodes in the controlled spark source.

A reference set of xenon arc spectra was photographed with the current to the source, the exposure time, and the width of the spectrograph slit being kept constant. The magnet and the sample in the sample cell in the magnet were pre-cooled to the operating temperature. The reference spectra were all taken with the magnetic field off, and each with different angles between the polarizer and the analyzer. At one of these angles, a single spectrum was photographed with the field on. Figure 10 is a photograph of a typical plate.

The angle between the polarized beam and the analyzer that was chosen for the "field on" spectrum was then taken as the "zero point." Since any vertical line in Figure 9 gave the same result for the rotation, this meant that any angle between polarizer and analyzer could be chosen to be the "zero point." In order to be able to measure rotations which might be negative as well as positive from the "zero point," the angle chosen was not the one for extinction of the transmitted beam (crossed polarizer and analyzer). The smaller the angle between the polarizer and the analyzer, the greater would be the intensity of the transmitted light, so it would seem that, since source intensity was often a
A TYPICAL PLATE

Figure 10
concern, it would be advantageous to choose a very small angle. However, since, as will be shown, the method involved interpolation between the microphotometer readings taken at the same wavelength of two successive reference spectra, it was necessary to keep the difference between the readings on two successive spectra as large as possible. To accomplish this an angle between polarizer and analyzer of nearly 90° had to be chosen as the "zero point."

To measure the rotation at a given wavelength, the microphotometer reading of the "field on" spectrum at that wavelength was compared with those of the reference spectra at the same wavelength. It was found that linear interpolation between successive values could be used as long as the reference spectra were taken at intervals of from 0.5° to 2.0° (intervals of less than 0.5° were impractical due to variations in source intensity during photographing). The accuracy of the values obtained in this way for the rotation of the plane of polarization depended on the interval size used in taking the reference spectra. For an interval of 2.0°, the values for the rotation were accurate to ± 1.0°.

Figure 11 shows the magneto-optical rotatory dispersion curve that resulted from the application of this method to a 10 cm sample of benzene. The reference spectra were taken at 5° intervals so that the values for rotation are accurate to ± 2.5°. Since no measurements of the field strength were taken for the 10 cm cell, the results of an experiment using a 1 cm sample of benzene in a known magnetic field were compared with these results, and by use of
10 CM BENZENE IN 1300 GAUSS

Figure 11
Verdet's Law the field was estimated to have been about 1300 gauss in the 10 cm sample. The sample cell was fitted with glass end plates so that all radiation of wavelength less than 325 μm was absorbed.

Figure 12 shows that this method can be successfully used to obtain rotatory dispersion curves for gases as well as liquids. The pole pieces were in position, and the field was about 3400 gauss, but no sample cell was placed in the magnet, so the curve is for the magneto-optical rotatory dispersion of air at a temperature slightly below room temperature and a pressure of about one atmosphere.

Figure 13 shows the result of measurements made with the 5 cm sample cell with the quartz end plates in place but only room air as a sample. These curves indicate that this method for studying the Faraday effect measures only magnetically induced rotation, even when natural optical rotation is present, as it is in the case of quartz. Since natural optical rotation does not depend on the direction of the magnetic field, the total rotation (natural plus magnetic) should be different if the field is reversed. The rotations measured by this method for equal and opposite fields were themselves equal and opposite which could only be true if magneto-optical rotation alone were being measured.

When greater blackening of the plates was needed, two methods were available in obtaining it. The source itself could not be made more intense, but since the method involved a photographic process, either the exposure time could be increased, or the spectrograph
**Figure 12**

- Rotation in degrees vs. Wavelength in millimicrons

**Figure 13**

- Rotation in degrees vs. Wavelength in millimicrons

**Figure 12**

- Quartz end plates in 3400 gauss and -3400 gauss

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slit could be widened, or both. The normal slit width was 100 μ.
Measurements of rotation made by using this slit width were com-
pared with measurements of the rotation using slit widths as large
as 750 μ, and it was found that for all areas that could be checked
the wider slits did not affect the accuracy of the values obtained.
The electromagnet presented a problem when exposure times of greater
than two minutes were attempted. Even though the magnet was water
cooled, with a current of greater than five ampere, the wire com-
partments would become sufficiently hot after two minutes to increase
the resistance causing a decrease in current and a drop in the
intensity of the magnetic field. This problem was overcome by taking
two or more exposures of the "field on" spectrum, and allowing the
magnet to cool for several minutes between exposures.
CHAPTER IV

THE RESULTS

Distilled Water

Figure 14 is a magnet-optical rotatory dispersion curve which was the result of an investigation of the Faraday effect in a 5 cm sample of distilled water. The magnetic field intensity was about 3150 gauss. Down to slightly less than 250 μm the relationship between the rotation and the wavelength has the general form

\[ \chi = \frac{A}{\lambda^p} \]

where \( \chi \) is the rotation, \( \lambda \) is the wavelength, and \( A \) and \( p \) are constants. Below 250 μm, however, the curve departs from this behavior and begins to decrease with decreasing wavelength. This effect is known as anomalous dispersion, and hereafter it will be referred to simply as a reversal of the dispersion curve. A previous study had indicated that one might be able to expect reversals in the wavelength region near an absorption band in the spectra of the sample.\(^{14}\) However, since water is not known to have an absorption band at this wavelength, the phenomenon was investigated further to see if it was real. It was found that the polarimeter was absorbing light at that wavelength, but since the polarimeter components were not in the magnetic field, it did not seem likely that they could have caused the anomalous dispersion. Since a similar reversal did
Figure 14

DISTILLED WATER IN 3150 GAUSS
5 CM SAMPLE
1 cm DISTILLED WATER IN 3000 GAUSS

Figure 15

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not occur at the high wavelength end of the curve, it was concluded that the reversal in the dispersion curve was not introduced by the photographic method of measuring rotation. The conclusion was that the effect was real, but due to the absorption by the polarimeter it could not be fully investigated.

Nickel Salt Solutions

The problem of finding an explanation of the strong reversal in the magneto-optical rotatory dispersion curve for distilled water suggested that an investigation of the nature of magneto-optical rotation in the vicinity of absorption bands be undertaken. Certain nickel salts in water solution are green in color and should have an absorption band in the blue section of the visible spectrum. Nickel sulfate (NiSO₄) and nickel chloride (NiCl₂) both have absorption bands which reach a maximum absorbency at about 400 mp. Figure 16 is an absorption spectrum for a 0.1 F (Formula weight) solution of nickel sulfate in water. Within the range of the SA3 plates, the magneto-optical rotation could be investigated in these solutions both above and below the absorption band. Figures 17 and 18 show dispersion curves for 5 cm samples of 0.25 F aqueous solutions of nickel sulfate and nickel chloride, respectively. The intensity of the magnetic field was in each case approximately 3000 gauss. The reversal of the dispersion curve appears again at the low wavelength end of the curve (probably due to the water), but a reversal of the curve also appears at the upper end of the absorption
Absorption spectrum for 0.1 F aqueous solution of nickel sulfate.

Absorption is $\log \frac{I}{I_0}$ where $I$ is the intensity of the transmitted radiation and $I_0$ is the intensity of the incident radiation.

Figure 16
5 CM 0.25 F NICKEL SULFATE IN WATER  
FIELD INTENSITY - 3000 GAUSS

Figure 17

Rotation in degrees

Wavelength in millimicrons

5 CM 0.25 F NICKEL CHLORIDE IN WATER  
FIELD INTENSITY - 3000 GAUSS

Figure 18

Rotation in degrees

Wavelength in millimicrons

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band (about 430 mp).

The spectrograph slit width was increased, and the exposure time was lengthened in an attempt to investigate the rotation in the absorption band. All experiments using the 5 cm cell were unsuccessful, however, so the 1 cm cell was tried. A series of solutions of nickel sulfate was prepared and studied in the 1 cm cell.

Figure 20 shows the curve for the 0.25 F aqueous solution of nickel sulfate. The sample path length was 1 cm, and the magnetic field intensity was about 5100 gauss. Note that in contrast with Figure 17 the curve did not show a reversal at the high wavelength edge of the absorption band. The curve is similar to the one in Figure 15, which is for 1 cm distilled water in a field of about 3000 gauss.

Figure 21 shows the curve for a 0.50 F aqueous solution of nickel sulfate. This curve displayed a slight "dip" in the dispersion curve in the region of the spectrum occupied by the absorption band.

Figure 22 displays the magneto-optical rotatory dispersion curve resulting from an investigation of a 1 cm sample of a 0.75 F aqueous solution of nickel sulfate in a magnetic field of about 5100 gauss. Not only is there a reversal from a curve which would have an appearance similar to that of the curve for distilled water, but at the wavelength of the center of the absorption band the sense of rotation becomes negative.
1 cm 0.25 F NICKEL CHLORIDE IN WATER
FIELD INTENSITY = 3000 GAUSS

Figure 19
1 CM 0.25 F NICKEL SULFATE IN WATER
FIELD INTENSITY - 5100 GAUSS

Figure 20
1 CM 0.50 F NICKEL SULFATE IN WATER
FIELD INTENSITY - 5100 GAUSS

Figure 21

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1 CM 0.75 F NICKEL SULFATE IN WATER
FIELD INTENSITY - 5100 GAUSS

Figure 22

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Figures 23 and 24 show the rotatory dispersion curves for 1.00 F and 2.00 F aqueous solutions of nickel sulfate, each at a magnetic field intensity of approximately 5100 gauss. In order to obtain the measurements of rotation in the absorption band of the 2.00 F solution it was necessary to use a spectrograph slit width of 750 μ and an exposure time of ten minutes.

According to Verdet, the concentration of salt in a solution could be determined by application of the Faraday effect. Figure 25 shows the magneto-optical rotatory dispersion curves for five different concentrations of nickel sulfate solution overlayed. All of these curves were taken from experiments carried out using the same magnetic field intensity. Within the accuracy of the experiments, the curves below the absorption band were identical, and with the exception of the 0.25 F solution the curves above the absorption band were also identical. At the center of the absorption band, the 0.75 F, 1.00 F, and 2.00 F solutions all displayed a reversal of the sense of rotation. The maximum negative rotation was the same for each of the three solutions.

Figure 26 shows the curve for 1 cm of the 1.00 F nickel sulfate solution taken with a magnetic field of approximately 3000 gauss superimposed on the curve taken from Figure 23 which was for the same concentration and path length, but for a magnetic field intensity of approximately 5100 gauss. The ratio of 3000 to 5100 is 0.59, and the average ratio of the rotation at a given wavelength of the 3000 gauss curve to that of the 5100 gauss curve at the same wave-
1 CM 1.00 F NICKEL SULFATE IN WATER
FIELD INTENSITY - 5100 GAUSS

Figure 23
OVERLAY OF FIGURES 20 THROUGH 24

Figure 25

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1 cm 1.00 F NICKEL SULFATE IN WATER

- Field intensity - 5100 gauss
- Field intensity - 3000 gauss

Figure 26
length is about 0.58 except in the range from 350 m\mu to 450 m\mu. Thus Verdet’s Law is not valid within the region of the absorption band. Another interesting fact concerning this figure is that the maximum negative rotation reached by the 1.00 F concentration was the same with both the 3000 gauss and the 5100 gauss magnetic fields.

An attempt was made to find another solvent for nickel sulfate. The Handbook of Chemistry and Physics lists alcohol as a solvent,\textsuperscript{16} but it was found impossible to dissolve any amount of nickel sulfate in ethyl, methyl, or iso-propyl alcohol at room temperature. It was possible to obtain a 0.25 F solution in 6.0 N ammonium hydroxide. Figure 27 shows the absorption spectrum for a 0.1 F solution of nickel sulfate in 6.0 N ammonium hydroxide. Figure 28 is the magneto-optical rotatory dispersion curves for both the 6.0 N ammonium hydroxide and the 0.25 F solution of nickel chloride in 6.0 N ammonium hydroxide. Both represent sample path lengths of 1 cm and magnetic field intensities of approximately 4500 gauss. It was not possible to maintain a stronger concentration than 0.25 F at the 17° C. operating temperature.

Other Salt Solutions

Preliminary investigations were carried out on three other salt solutions using the 5 cm cell. The three salts were cobalt chloride (CoCl\textsubscript{2}), copper sulfate (CuSO\textsubscript{4}), and zinc sulfate (ZnSO\textsubscript{4}). The absorption band of the zinc sulfate solution was in the region of
Absorption

Absorption spectrum for 0.1 M solution of nickel sulfate in 6.0 N ammonium hydroxide

Figure 27

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1 CM AMMONIUM HYDROXIDE AND
1 CM 0.25 F NICKEL SULFATE IN AMMONIUM HYDROXIDE
FIELD INTENSITY - 4500 GAUSS

Figure 28

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the spectrum where absorption by the polarimeter would have made investigation of the magneto-optical rotation impossible.

Figure 29 shows the dispersion curve obtained from a 5 cm sample of a 0.5 F aqueous solution of cobalt chloride in a magnetic field of about 3100 gauss. The edge of the absorption band is at approximately 450 mp. The reversal of the dispersion curve at the low wavelength end of the spectrum is due to the water.

Figure 30 is the magnetic rotatory dispersion curve for a 5 cm sample of a 1.0 F aqueous solution of copper sulfate in a magnetic field of approximately 3100 gauss. The upper edge of the absorption band is about 340 mp. A definite reversal of the dispersion curve is seen at this edge of the absorption band.

Figure 31 shows the magneto-optical rotatory dispersion curve for a 5 cm sample of a 1.0 F aqueous solution of zinc sulfate in a magnetic field of about 3100 gauss. This solution is transparent through most of the range of the SA3 plates.

Benzene

An attempt was made to study the magneto-optical rotation in the absorption band of benzene. Figure 32 shows the dispersion curve resulting from a 1 cm sample of benzene in a magnetic field of about 4800 gauss. There is a sharp reversal of the curve at the high wavelength edge of the absorption band, but the absorption is so strong that all attempts to study the rotation in this band were unsuccessful. Previous work had demonstrated that benzene and
Figure 29.

5 CM 0.5 F COBALT CHLORIDE IN WATER
FIELD INTENSITY - 3100 GAUSS

Figure 30.

5 CM 1.0 F COPPER SULFATE IN WATER
FIELD INTENSITY - 3100 GAUSS

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5 cm 1.0 F ZINC SULFATE IN WATER
FIELD INTENSITY = 3,100 GAUSS

Figure 31

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1 cm BENZENE IN MAGNETIC FIELD OF 4800 GAUSS

Figure 32
cyclohexane, when mixed, gave dispersion curves that appeared to be additive with respect to the percentage of each in the mixture. Two solvents for benzene were tried. The first was iso-propyl alcohol. Figure 33 shows two magnetic rotatory dispersion curves, the one being for iso-propyl alcohol, and the other for a mixture containing ten percent benzene (by volume) in iso-propyl alcohol. Although iso-propyl alcohol is transparent down to at least 250 μ, the mixture absorbed very strongly in the region of the benzene absorption band.

The second solvent that was tried with benzene was n-heptane. Figure 34 shows the dispersion curve for a 5 cm sample of n-heptane along with the curve for a 5 cm sample of a mixture containing ten percent (by volume) benzene in n-heptane. Again, the strong absorption of the benzene in the mixture prevented the study of the magneto-optical rotation at wavelengths less than 270 μ.

Figure 35 shows the rotatory dispersion curve for a 5 cm sample of 3-methyl-hexane, an isomer of n-heptane. N-heptane has a molecule which contains a chain of seven carbon atoms. 3-methyl-hexane has one of the carbon atoms on the side, so that there are only six carbon atoms in the chain. The rotation for 3-methyl-hexane was slightly less than that for n-heptane at each wavelength.
1 CM ISO-PROPYL ALCOHOL AND 1:CM BEZENE
ISO-PROPYL ALCOHOL MIXTURE

Field Intensity = 5100 gauss

- iso-propyl alcohol
- 10% benzene, 90% iso-propyl alcohol

Figure 33

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5 CM N-HEPTANE AND 5 CM BENZENE N-HEPTANE MIXTURE

Field Intensity - 4000 gauss

- ○ - n-heptane
- ▲ - 10% benzene, 90% n-heptane

Rotation in degrees

Wavelength in millimicrons

Figure 34

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5 cm 3-METHYL-HEXANE IN 4000 GAUSS

Rotation in degrees

Wavelength in millimicrons

Figure 3S

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CHAPTER V

CONCLUSIONS

A method for studying magneto-optical rotation in the ultraviolet range of the spectrum has been developed and successfully implemented to obtain several interesting results. The method uses the spectrograph, and data are recorded on photographic plates. This method has several advantages over methods which utilize the spectrometer and electronic equipment for the recording of data.\(^{12}\)

1. The photographic plates provide permanent storage for data.

2. More accurate measurements of the rotation of the plane of polarization can be obtained.

3. The photographic plates are more sensitive in the ultraviolet range of the spectrum.

4. The length of time that the electromagnet must remain on is shorter which allows magnetic fields of greater intensity to be obtained.

5. The use of wide spectrograph slit openings and long exposure times allows magneto-optical rotation in absorption areas to be studied.

The disadvantage of this method compared to those methods using electronic recording of data are that much more time is required to obtain the measurements of the rotation.

The results of the application of this method to a study of aqueous solutions of nickel sulfate are very interesting.

1. The concentration of nickel sulfate in the solution cannot be determined by use of the Faraday effect.
(2) Verdet's Law is not valid at the wavelengths corresponding to an absorption band.

(3) Anomalous dispersion occurs in the absorption band.

(4) Magneto-optical rotation is related to the presence of the nickel ion.

(5) The magneto-optical rotation in the absorption band is related to the total number of ions in the light path.

The magneto-optical rotatory dispersion curves for nickel sulfate and nickel chloride (5 cm samples and 1 cm samples of 0.25 F aqueous solutions) are identical within the accuracy of the experiments leading to the conclusion that the nickel ion is related to the magnetic rotation. The curve for 5 cm of 0.25 F nickel sulfate gave indication of a strong reversal in the region of the absorption band, but with the 1 cm cell, only the 0.75 F, and stronger solutions displayed this effect. Thus it is concluded that the effect must be related to the total number of nickel ions in the light path rather than the density of ions. It was also interesting that for all those solution which exhibited the strong reversal of the dispersion curve in the absorption band, the minimum values of rotation were the same, even when a different magnetic field was applied.

The amount of rotation of the plane of polarization by the carbon chain molecules seems to depend on the length of the chain. Since there were no absorption regions in the spectrum of either n-heptane or 3-methyl-hexane (in the range of study by this method), it was impossible to see if the magneto-optical rotation in these areas would provide any insight into their molecular structures.
Future experimentation with this method could profitably be applied to the study of magneto-optical rotation in the vicinity of absorption bands. The results included here suggest that the rotation of the plane of polarization of polarized light at those wavelengths corresponding to absorption bands might contribute to a better understanding of the structure of molecules. This method, although it is slow, provides an effective way to study the Faraday effect in areas of the spectrum where there is strong absorption of incident radiation by a sample.
BIBLIOGRAPHY


16. loc. cit., p. 615.