A METHOD OF MEASUREMENT OF THE FLOW BIREFRINGENCE OF A THIN FLUID LAYER IN OSCILLATORY SHEAR

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PREFACE

The apparatus, the mathematical relations, and the experimental techniques for the measurement of the dynamic optical properties of flow-birefringent fluids subject to sinusoidal shear are discussed in this paper. Sample data obtained using aqueous solutions of milling yellow dye are presented. The purposes of the work were to evaluate the test apparatus as a means of measuring the dynamic optical properties, to establish a convenient mechano-optic relation for the presentation of data, and to measure the dynamic optical properties for a milling yellow solution to provide a sample of the measurements to be obtained from the apparatus.

The author wishes to express his appreciation to Dr. G. B. Thurston for the many helpful suggestions and invaluable guidance provided throughout the course of the investigation, to Mr. Richard Ely for making comparison measurements of the rigidity and viscosity of the milling yellow solutions, and to Mr. Heinz Hall and Mr. Frank Hargrove for the excellent work done in constructing the test apparatus.

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CHAPTER I

INTRODUCTION

Most molecules in a fluid are optically anisotropic, since their electrical polarizabilities are usually different in different directions. In the fluid, however, the molecules (or aggregates of molecules) are randomly oriented, due to thermal agitations. Hence, although a fluid may have optically anisotropic molecules, the anisotropy is hidden until some orientation of the molecules takes place. This orientation may be accomplished electrically, magnetically or hydrodynamically. The latter, which gives rise to the effect known as the Maxwell effect, is usually studied from the standpoint of steady two-dimensional flow. Such a flow will produce an orientation of particles, as well as causing a certain degree of deformation of the molecules. There still is some question as to whether the orientation of anisotropic molecules, the deformation of isotropic molecules, or some combination of both effects, is responsible for the optical anisotropy of some fluids.

In 1866 Maxwell noted that the state of strain of a fluid might be detected by its action on polarized light. In 1873[1] he described the effects exhibited when Canada balsam was placed between crossed polarizers and excited by a spatula moving up and down in its own plane in the fluid. He also described a concentric cylinder apparatus in which the flow birefringence could be produced more readily. By this time the relation between the optical interference pattern and the motion of the fluid was being sought by several investigators. In 1874 Kundt published the first real attempts to get quantitative data and a correlating theory.[2] His work was based on the work by Stokes, in which Stokes treated incompressible viscous fluids. Kundt indicated that the stresses in the fluid were the cause of the optical anisotropy, and he assumed that the optic axes of the liquid would coincide with the principal stress axes. This would indicate a constant orientation of the optic axes in steady flow, and hence a constant extinction angle χ, where χ is defined as the angle between the flow streamlines in the fluid and the optical axes of the fluid.

$$\Delta n = K \Upsilon G \tag{1.1}$$

where

Δn = difference in indices of refraction

K = a constant

Υ = the relaxation time of the liquid

G = the velocity gradient in the fluid.

The experiments performed indicated that χ did vary with the velocity gradient for several fluids, contrary to Kundt's prediction. In 1888 De Metz[3] found that the amount of birefringence exhibited by a fluid decreased with increasing temperature. Natanson and Zaremba then attempted to improve the relation set forth by Kundt, but with little success. Later Natanson,[4] assuming that the stress caused the optical anisotropy, obtained the expression for the extinction angle

$$\cot 2\chi = \pm \Upsilon G \tag{1.2}$$

where Υ and G are as defined previously.

Many other relations were proposed, some introducing the effects of particle size and shape. However, it was not until 1928 when Raman and Krishnan[5] put forth their theories of particle orientation that a fairly good description of some of the experimental data was provided. They assumed that the effect of the tensile and compressive forces was to produce an orientation of the assymetric molecules instead of producing strain double refraction. They assumed that the molecules would orient themselves with their largest molecular dimension along the direction of tension. The orientation would be opposed by the thermal agitations, and hence the orientation measured would be a statistical equilibrium between the two effects. The resulting expression for the optical anisotropy is

$$\frac{\Delta n}{n \eta G} = [M] \qquad (1.3)$$

where

$[M]$ = a constant called the Maxwell constant for the fluid

Δn = the difference in indices of refraction for the flowing fluid

n = static index of refraction for the fluid

η = steady flow viscosity of the fluid.

The theory thus predicted again a constant χ , which was contradictory to some experimental evidence. It did predict, however, that Δn would be directly proportional to η and G and thus a decreasing Δn corresponding to an increasing temperature would be explained by the decreasing η of the fluid. In 1941 the relation was shown to be good for low molecular weight liquids, such as benzene and the alcohols, which exhibited a constant extinction angle.[6] Several other theories have been presented since, and most have been found to be at least partially adequate for some specific type of fluid. For example, Haller[7] treated the case of rigid particles, while Boeder[8] dealt with colloidal solutions. W. Kuhn[9] considered the particles to be either optically anisotropic and rigid, or isotropic and flexible. The later theories of Sadron, of Peterlin and Stuart, and of Snellman and Bjornstahl are highly complex and will not be discussed here,[10] other than to note that liquid solutions have been found that exhibit the behavior predicted by these various theories. A. S. Lodge[11] has shown that if one assumes that the same mechanism gives rise to the birefringence and the stress in a flowing fluid, and if one assumes that the stress and the birefringence originate in network deformation in the fluid, then in shear flow

$$\frac{\Delta n}{\Delta p} = \frac{\Delta n \sin 2\chi}{2G(\eta - \eta_0)} \tag{1.4}$$

where

Δp = difference in the principal stresses in the fluid
η = solution viscosity
η_0 = solvent viscosity.

This relation has been verified for certain polymer solutions.[11] However, none of these theories has been shown to hold for all fluids in steady flow as of yet. Note also that all of these theories are based on an equilibrium situation, in which the velocity gradient is invariant with time.

Most of the static stress analysis work done utilizing birefringent solids utilizes the Maxwell relation for elastic solids[12] for which

$$\Delta n = C \Delta T \tag{1.5}$$

where

C = relative stress-optic coefficient

ΔT = difference in the principal stresses in the material.

Some investigators use a relation of the form of the Neumann relation,[12] for which

$$\Delta n = \frac{u}{v_0^2}(q-p)(S_r - S_t) \tag{1.6}$$

where

u = velocity of light in vacuo

v_0 = velocity of light in the unstrained material

$(q-p)$ = strain optical coefficient

$(S_r - S_t)$ = difference in principal strains.

Since for static loading there can be no phase difference between stress and strain and only the magnitudes will differ, it is somewhat arbitrary as to which relation is used. This will not be true for time-varying stresses, however.

A considerable amount of work also has been done in an attempt to calibrate a system using birefringent fluid for measurements of local velocity gradients in fluids in two-dimensional flow. In 1923 Humphry[13] tried vanadium pentoxide sol for such studies. In 1935 Alcock and Sadron[14] made similar calculations using sesame oil. Dewey[15] utilized bentonite sols for lengthy studies of flow phenomena and presented his findings in his doctoral dissertation in 1941. In 1942 Weller[16] presented a similar analysis, in which many liquids were tried. More recently, Balint[17] and Rosenberg[18] have reviewed and extended the work of Dewey and Weller. In 1953 a new fluid was found for birefringence measurements, an aqueous solution of milling yellow dye, a product of National Aniline Division of

Allied Chemical and Dye Corporation. A description of the flow birefringence and the rheological properties of milling yellow has been presented by Prados, Peebles and Honeycutt in Office of Naval Research Contract Nonr-811(04) reports.[19, 20, 21, 22]

In 1957 Hargrove and Thurston described studies in which aqueous milling yellow solutions were used to study sinusoidal flow through orifices.[23] Later, results were presented for the propagation of plane waves through a milling yellow solution, treating it as a viscous fluid.[24] This work was undertaken to determine the mechano-optic relation for fluids undergoing a sinusoidal time variation in flow or in shear, where the fluid was not in an equilibrium situation. The shear studies were studies of the propagation of plane transverse waves in milling yellow solution and were restricted to studies of the "zero order fringes"--the areas in the fluid exhibiting no birefringence at a given instant of time.

The work presented here was done using a system in which a plane oscillating sinusoidally in its own plane was used to produce shear in an aqueous milling yellow solution placed between the plane and a closely spaced stationary parallel plane reflector.

The purposes of this study were to establish the system as a method of measurement of the dynamic optical properties of fluids, to develop a mechano-optic relation adequate for the analysis of the data obtained from the dynamic measurements, and to study a particular fluid, a milling yellow dye solution, to provide an example of the applicability of the system and the mechano-optic relation for studies of birefringent fluids. Hence, discussions of the test system and the mechano-optic relation used are presented, along with data obtained for aqueous milling yellow solutions. The milling yellow studies were made as functions of temperature, concentration, and frequency.

The test system appears to be adequate for the measurement of the dynamic optical properties of birefringent fluids. However, no other work is available to provide a cross check on the system. The mechano-optic relation presented provides one with a convenient method for the analysis of the experimental data. The milling yellow measurements seem to indicate that there is a relation between the rigidity and the optical sensitivity of the fluid. Also, the temperature and concentration measurements indicate that high temperatures correspond fairly well to low concentrations, and low temperatures to high concentrations.

CHAPTER II

THEORY

A. The Flow-Optic Relation

Many books and articles treating the rheological properties of fluids give a general treatment of the phenomena called streaming or flow double refraction.[6] A flow-birefringent fluid is one that exhibits anisotropy of velocity of propagation of light with direction of propagation and plane of polarization when the fluid is flowing. When the fluid is at rest, it is optically isotropic. That is, the index of refraction of the fluid is independent of direction of propagation and plane of polarization of the incident light ray when the fluid is at rest. In flow, however, the internal stresses and velocity gradients cause the fluid to become optically anisotropic temporarily.

Consider the path of a ray of light passing through a moving fluid element in a direction perpendicular to the direction of motion of the fluid. There will be two mutually perpendicular orientations of the electric vector for an incoming ray for which the electric vector will undergo no rotation due to passage through the medium.

The velocities of propagation C_I and C_{II} associated with these two orientations of the electric vector differ, however. That is, the medium exhibits different indices of refraction for the two orientations of the electric vector. If the electric vector should have an orientation in a direction other than one of these two directions, the medium will effectively resolve the vector into its components along these directions. The components will then propagate through the liquid with differing velocities C_I and C_{II}. The emerging components then will combine to give plane polarized, elliptically polarized, or circularly polarized light, depending on the length of the path of propagation. As is shown in figure 1, the orientation of the electric vector **E** entering the medium is established by the polarizer. The analyzer, oriented perpendicular to the polarizer, will then transmit any component of the emergent beam having the proper electric vector orientation. Hence, the light emerging from the analyzer will reflect directly the degree of rotation produced by the medium. For a more rigorous analysis of flow birefringence see <u>Optics</u>, by Born and Wolf.

To express the effect quantitatively, consider the following. Assume that the light ray passing through the polarizer is given by

$$E = A \sin \frac{2\pi}{\lambda}(ct - \chi) \tag{2.1}$$

where

E = magnitude of the electric vector
A = amplitude
λ = wavelength
χ = arbitrary phase retardation to indicate that E is not necessarily zero at $t = 0$
t = time
c = velocity of light in vacuo.

Then the equations for the two resulting components I and II of the

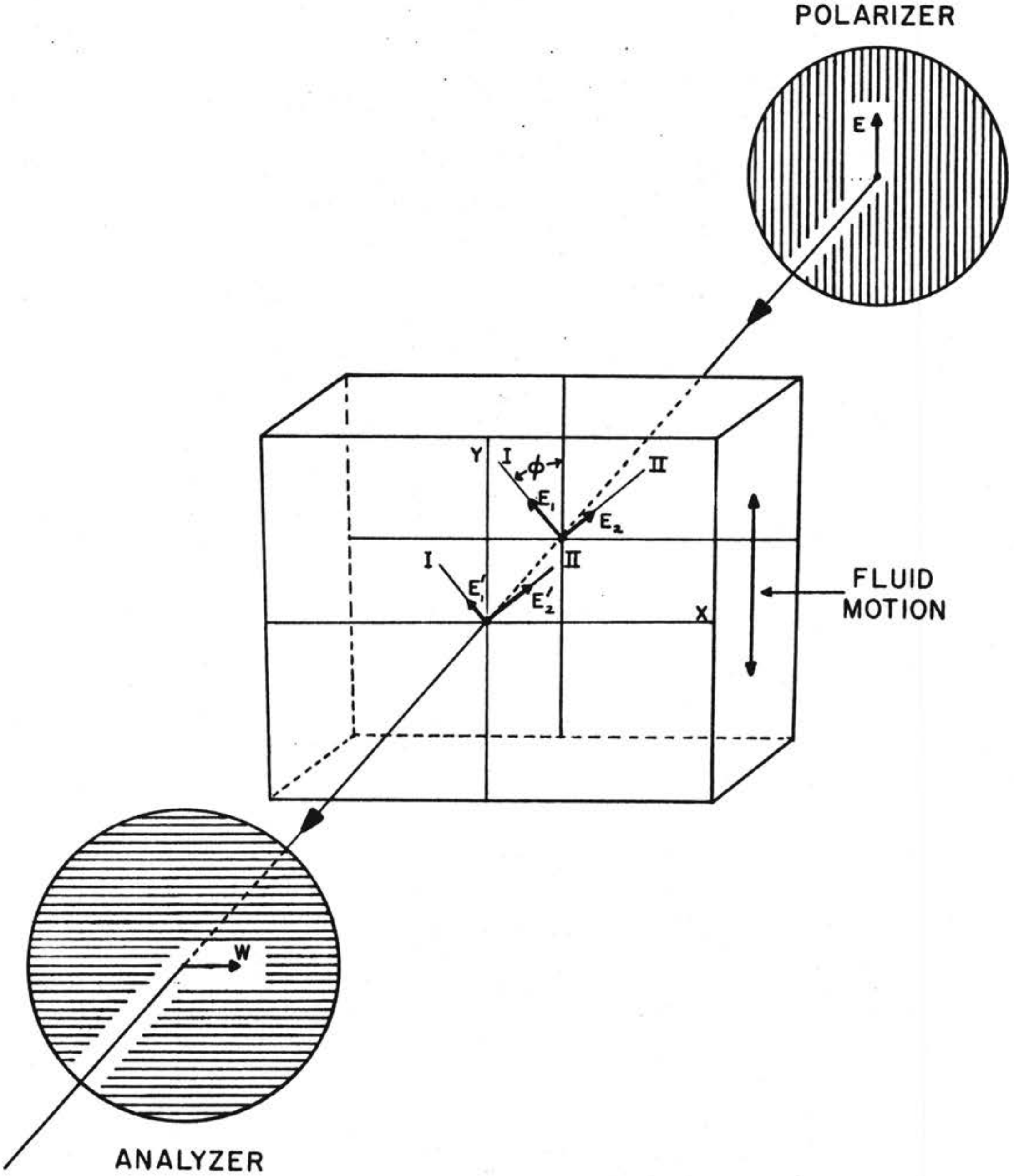

Figure 1. A schematic representation of plane polarized light passing through an element of flow-birefringent fluid.

light as it enters the flow-birefringent fluid are

$$E_1 = A \cos\phi \sin \frac{2\pi}{\lambda}(ct - x) \tag{2.2}$$

and

$$E_2 = A \sin\phi \sin \frac{2\pi}{\lambda}(ct - x) \tag{2.3}$$

where

E_1 = component of the electric vector in direction I

E_2 = component of the electric vector in direction II

ϕ = angle between I and Y.

These two components then travel through the fluid, one travelling with velocity C_I, the other with velocity C_{II}. As a consequence, one will emerge a distance δ behind the other. The emergent components E_1' and E_2' will thus be given by

$$E_1' = A \cos\phi \sin \frac{2\pi}{\lambda}(ct - x) \tag{2.4}$$

and

$$E_2' = A \sin\phi \sin \frac{2\pi}{\lambda}(ct - x - \delta) \tag{2.5}$$

where

E_1' = component of electric vector having direction I, leaving the flow-birefringent fluid

E_2' = component of electric vector having direction II, leaving the flow-birefringent fluid

δ = relative retardation produced by passage through the fluid.

When E_1' and E_2' reach the second polarizer, only the component of the electric vector parallel to X is transmitted. Hence, the light transmitted through the analyzer will be the resultant of the components of and E_2' parallel to X. This resultant W will be given by

$$W = E_1' \sin \phi - E_2' \cos \phi \tag{2.6}$$

Substituting the values for E_1' and E_2' given by equations (2.4) and (2.5) and simplifying, one obtains

$$W = \left[A \sin 2\phi \sin \frac{\pi \delta}{\lambda} \right] \cos \frac{2\pi}{\lambda}\left(ct - x - \frac{\delta}{2}\right) \tag{2.7}$$

Note that $\left[A \sin 2\phi \sin \frac{\pi\delta}{\lambda} \right]$ is the amplitude factor for the resultant electric vector. Since the intensity of the transmitted light is proportional to the square of the amplitude, it is seen that the intensity of the emerging beam will be zero when

$$\left[A \sin 2\phi \sin \frac{\pi \delta}{\lambda} \right]^2 = 0 \tag{2.8}$$

This expression will be zero when

$$\phi = \frac{N\pi}{2}, \quad N = 0, 1, 2, \cdots \tag{2.9}$$

and when

$$\frac{\delta}{\lambda} = N, \quad N = 0, 1, 2, \cdots \tag{2.10}$$

Thus zero resultant intensity occurs where

1) direction I is some integral multiple of $\frac{\pi}{2}$, and hence is

either parallel or perpendicular to the transmission direction of the polarizer, or

2) the relative retardation δ produced by the passage of the light ray through the flow-birefringent fluid is a distance equal to an integral number of wavelengths of the incident light ray.

Consider further the second condition for zero resultant intensity of the transmitted light. The velocities of the component rays are given by

$$c_{II} = \frac{c}{n_{II}} \tag{2.11}$$

and

$$c_{I} = \frac{c}{n_{I}} \tag{2.12}$$

Assume that n_I is greater than n_{II}. Then component I will emerge from the fluid somewhat later than component II. This small time interval will be

$$\Delta t = \frac{\ell}{c/n_I} - \frac{\ell}{c/n_{II}} = \frac{\ell}{c}(n_I - n_{II}) \tag{2.13}$$

where

Δt = time interval between the emergence of components I and II

ℓ = length of path through the fluid

Since the velocity of light in air is approximately equal to the velocity of light in vacuo, the retardation distance δ will be given by

$$\delta = c\,\Delta t = \ell(n_I - n_{II}) = \ell \Delta n \tag{2.14}$$

where the factor $(n_I - n_{II}) = \Delta n$ is called the amount of birefringence or double refraction.

As was noted in Chapter I, almost all of the work done on fluids in steady flow has utilized some relation between the double refraction and the velocity gradient in the fluid. Peterlin states that for steady flow, Δn is a function of the velocity gradient,^{6} the expression of the function varying from one type fluid to another. Hence, assume a mechano-optic relation of the form

$$n_e - n_o = \Delta n = S^* \frac{\partial \dot{\xi}}{\partial x} \tag{2.15}$$

where $S^* = Se^{i\theta_s}$ is the complex optical coefficient, measurements of which are presented in Chapter IV.

Then, from equation (14),

$$\delta = l \Delta n = l S^* \frac{\partial \dot{\xi}}{\partial x} \tag{2.16}$$

B. The Closely Spaced Plane and Reflector

Consider the situation shown in figure 2. A plane, infinite in extent in the Y, Z directions, is oscillated in its own plane in the Y direction. A rigid, stationary reflector is placed close to the plane, at a distance D from the plane. Assume that this system is immersed in a fluid capable of supporting shear stress. Assume that for a fluid capable of supporting a transverse wave of wavelength λ the distance D is adjusted so that

$$\frac{\lambda}{D} > 10 \tag{2.17}$$

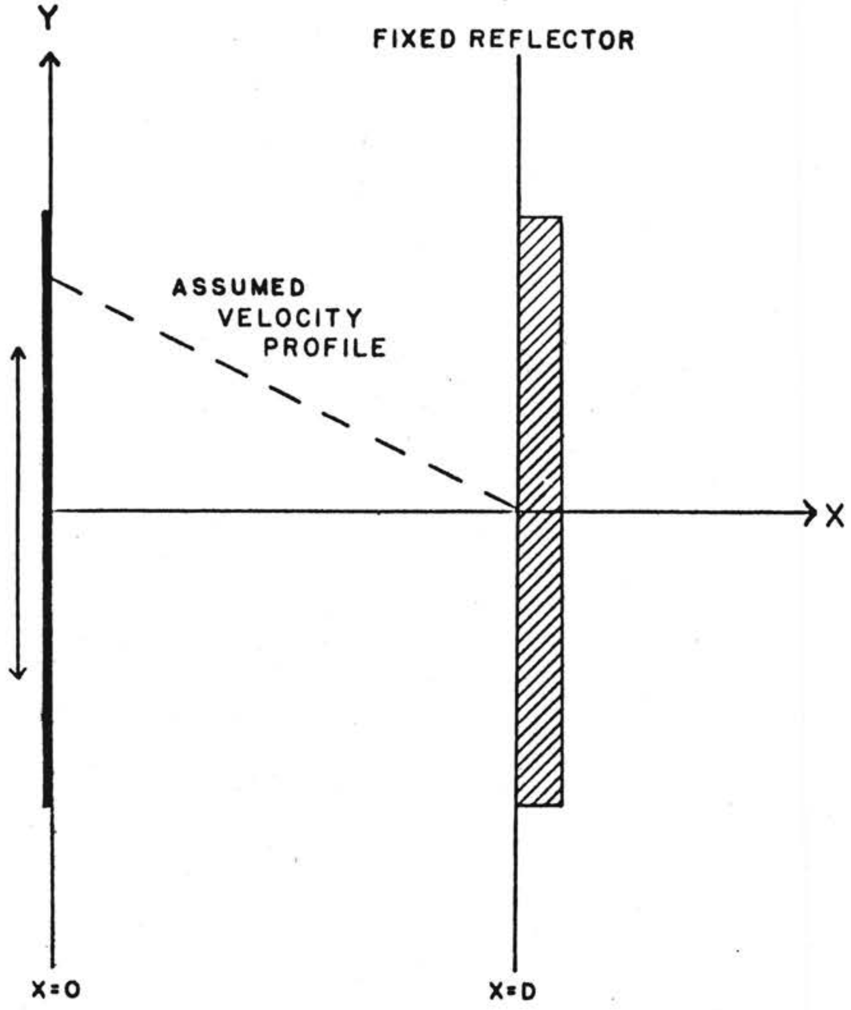

Figure 2. A pictorial representation of the oscillating plane, the fixed reflector, and the assumed velocity profile.

The velocity distribution in the gap between the plane and reflector will be approximately linear for the case specified by equation (2.17). Hence, if the plane motion is given by the real part of

$$\dot{\xi}_0 = \dot{\xi}_m \exp.(i\omega t) \tag{2.18}$$

where

$\dot{\xi}_0$ = velocity of the plane in the Y direction

$\dot{\xi}_m$ = peak velocity of the plane

$i = [-1]^{\frac{1}{2}}$

ω = angular frequency of oscillation

t = time.

Then the motion at some point x in the gap will be given by

$$\dot{\xi}_x = \dot{\xi}_m \left(\frac{D-x}{D}\right) \exp(i\omega t), \tag{2.19}$$

if it is assumed that no slippage occurs at the plane or the reflector. Thus the velocity gradient will be

$$\frac{\partial \dot{\xi}_x}{\partial x} = \dot{\xi}_m \left(-\frac{1}{D}\right) \exp(i\omega t) = -\frac{1}{d}\, \dot{\xi}_0 \tag{2.20}$$

C. The Flow-Optic Relation and the Closely Spaced Plane and Reflector

The relation between Δn and the velocity gradient to be used here was presented in equation (2.16). Applying equation (2.16) to the case of the closely spaced plane and reflector, the optical retardation becomes

$$\delta = \ell\, S^* \frac{\partial \dot{\xi}_x}{\partial x} = \frac{-\ell\, S\, \dot{\xi}_m}{D} \exp\left[i(\omega t + \theta_s)\right] \tag{2.21}$$

Taking the real part of equation (2.21) one has

$$\delta = -\frac{l S \dot{\xi}_m}{D} \cos(\omega t + \theta_s) \tag{2.22}$$

Note that for the optical system considered (See figure 1), no distinction can be made between the cases $n_{II} > n_I$ and $n_{II} < n_I$. Also, the ordinary and extraordinary axes cannot be identified, nor can the value of θ_s from equation (2.22) be determined to more than $\theta_s \pm \pi$. The sign of the cosine term of equation (2.22) could be determined utilizing an external compensator, but the ordinary and extraordinary axes would still remain unidentified. Hence, the sign of the Δn term would be meaningless, since $(n_e - n_o)$ might be either positive or negative, depending on the fluid studied. So, for the work presented here, one need consider only the absolute value of δ .

$$|\delta| = \frac{l S \dot{\xi}_m}{D} \left| \cos(\omega t + \theta_s) \right| \tag{2.23}$$

For solutions of sensitivities such that the $|\delta|$ may be adjusted to the condition

$$|\delta| = N\lambda, \; N = 1, 2, 3, \cdots \tag{2.24}$$

the relation between the plane velocity and the optical effect will be given by

$$\frac{l S \dot{\xi}_m}{N \lambda D} = \left| \sec(\omega t + \theta_s) \right| \tag{2.25}$$

The experimental methods for the determination of the dynamic optical coefficient S^* and its variation as a function of various parameters are discussed in the following chapter.

CHAPTER III

EXPERIMENTAL METHODS

A. Experimental Apparatus

The experimental apparatus used in this study consists of a brass plane, 3/4" x 3/4" x 1/4", oscillated in its own plane by a geophone type driver, and a stationary brass reflector spaced .011 inch away from the plane and parallel to it. Figure 3 is a photograph of this apparatus. The plane and reflector are submerged in fluid as indicated in figure 4. The shaft carrying the plane was fitted into a honed bearing in the base of the test chamber. All parts of the cell that come in contact with the fluid are made of brass or glass. The test cell was isolated thermally from the rest of the system by insulated hold-down screws and plastic washers between the upper plate and the test cell. The velocity of the plane was monitored by an electromagnetic unit of the geophone type, coupled to the plane shaft. The velocity monitor was calibrated from measurements of its electrical output voltage and determinations of its extremes of excursion measured visually with a telescope equipped with a bifilar eyepiece. The velocity monitor output was measured with a Ballantine Model 643 vacuum tube voltmeter.

The system was driven sinusoidally by a Hewlett-Packard Model 505AG Audio Oscillator for frequencies above 20 cps, and by a Hewlett-Packard Model 200CD Oscillator for frequencies from 20 to 10 cps. The output of the driving oscillator was fed to a constant impedance step

FIGURE LEGEND

Figure 3. A photograph of the test cell

A. Polarizer
B. Test cell (brass)
C. Oscillating plane (brass)
D. Reflector (brass)
E. Analyzer

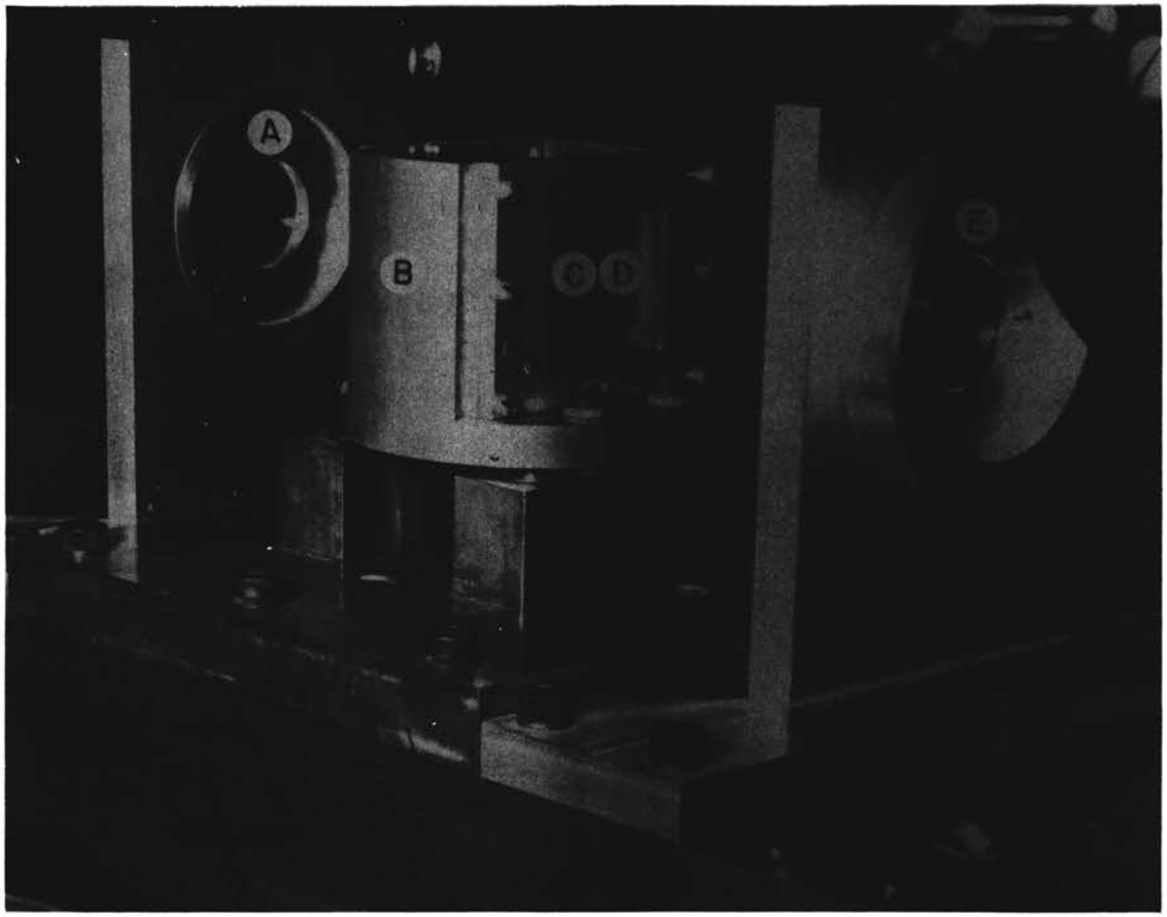

Figure 3

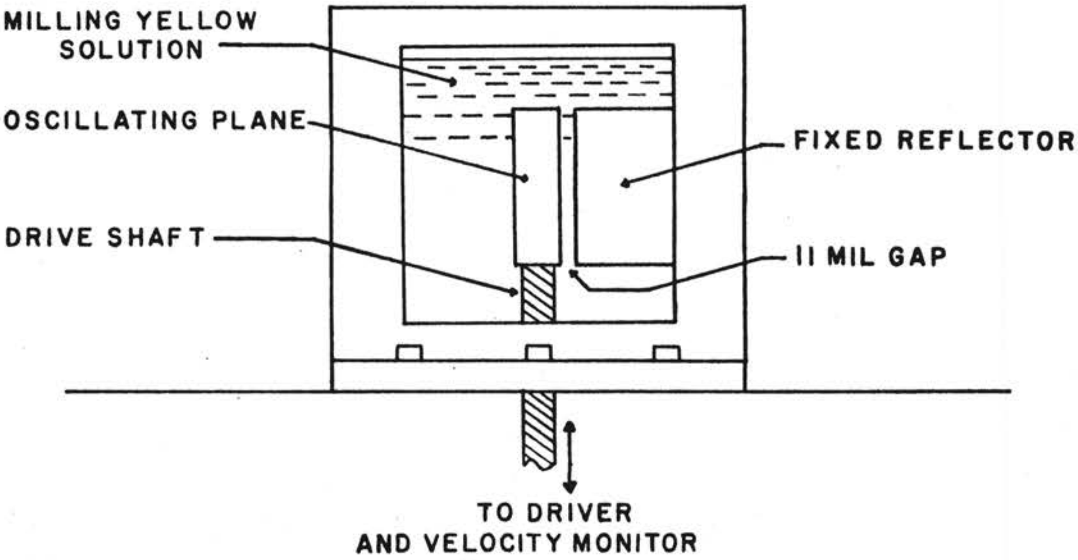

Figure 4. A simplified diagram of the test cell.

attenuator which in turn fed a continuously variable attenuator having a constant input impedance of 250 ohms, which fed the geophone driver. Hence, the amplitude of the plane motion could be controlled continuously without causing any change in the output voltage of the oscillator.

The stroboscopic illumination for the system was provided by a General Radio Type 1531A Strobotac. The Strobotac was triggered externally by a phase shift-trigger circuit network (See figure 5) which was coupled to the oscillator. This provided the necessary trigger pulse to synchronize the stroboscope with the plane motion, as well as allowing one to view the gap at any part of the cycle by an appropriate adjustment of phase. The light from the Strobotac was fed into the test system as shown in simplified form in figure 6. As is shown there, the light was incident on a .001 inch slit, oriented vertically, and a lens and interference filter were used to provide a monochromatic image of the gap in the opening between the oscillating plane and reflector. For the measurements made here, the central wavelength of the filter was 5780 Angstroms, and the bandwidth was approximately 80 Angstroms. By setting the lens f-stop to f32, it was possible to obtain an image that was less than .008 inch wide anywhere in the .011 inch gap between plane and reflector. Thus, by careful positioning of the lens, one could eliminate any reflections of the light beam from the plane or reflector. Crossed polaroids were positioned as shown and could be rotated to any orientation desired. For all measurements except extinction angle measurements the polarizer axis was oriented vertically. The gap was viewed through a Gaertner telescope.

A photocell circuit (See figure 7) was utilized to determine the instant at which the stroboscope flashed. The circuit produces a sharp

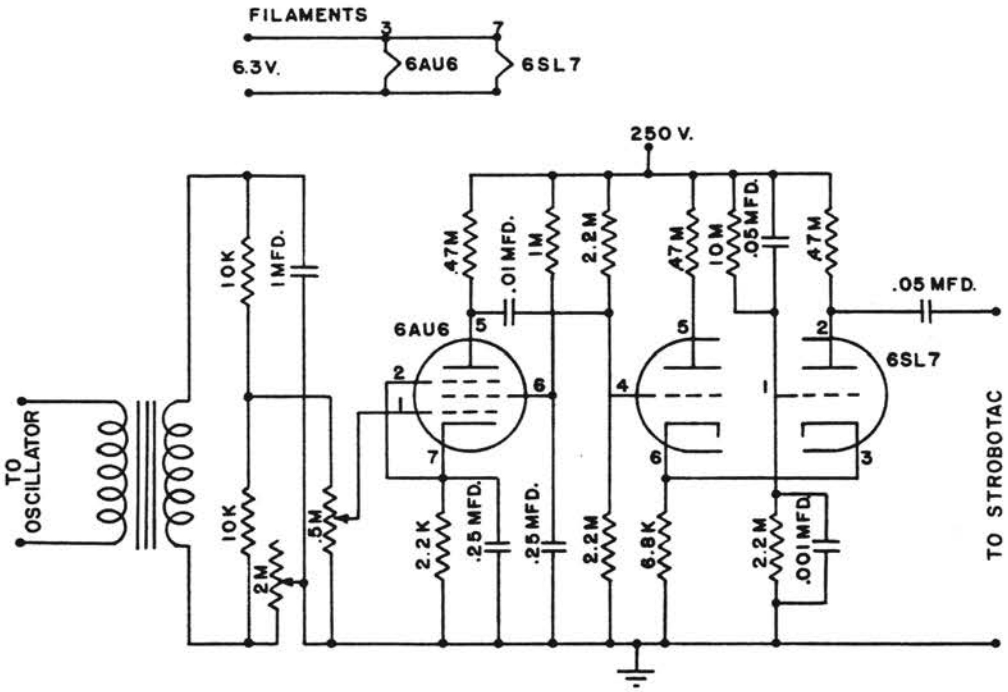

Figure 5. Schematic diagram of the variable phase synchronous trigger circuit.

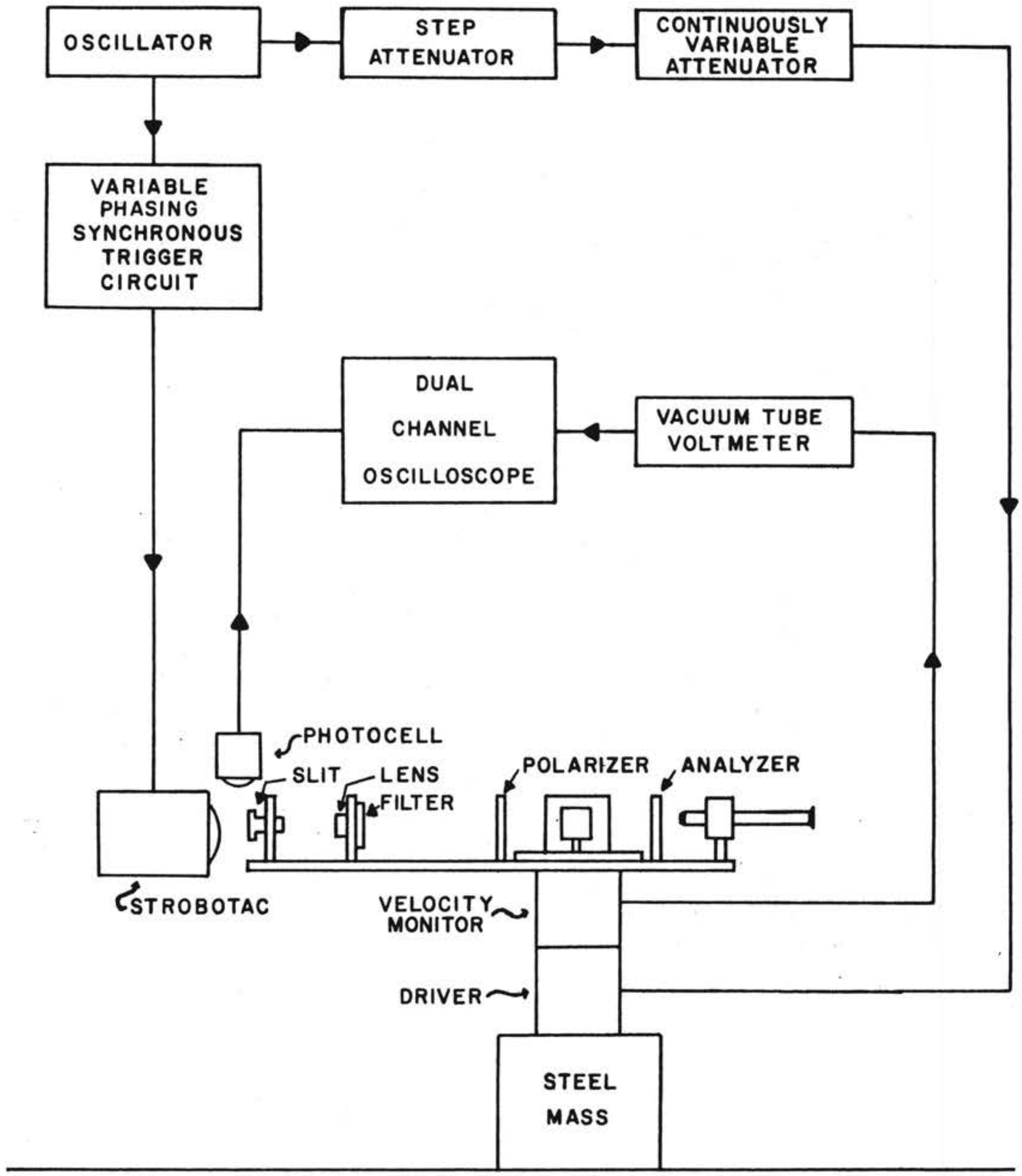

Figure 6. Simplified drawing of the test system and the associated electronic equipment.

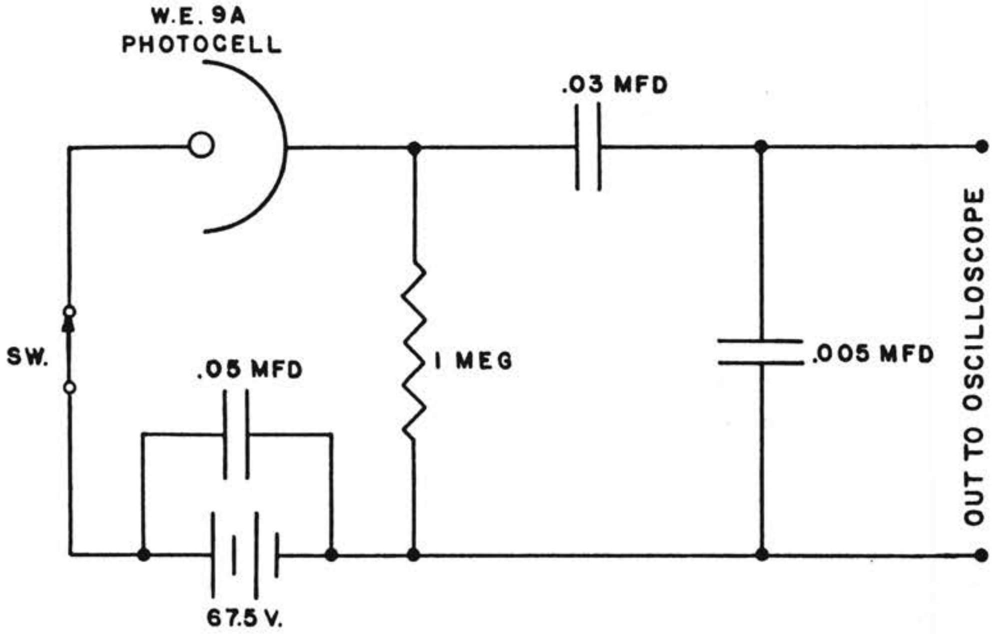

Figure 7. Schematic diagram of the photoelectric sensing device.

electrical pulse corresponding to the instant at which it is illuminated by the Strobotac. The outputs of this photocell circuit and the velocity monitor were then presented on a Hewlett-Packard Model 122A Dual Trace Oscilloscope, so that the phasing of the light pulse with respect to the plane velocity could be measured by visual inspection.

The entire system was mounted on a 160 lb. steel mass to eliminate motions of the entire system. The mass was isolated from the supporting table by rubber spacers to reduce the mechanical noise fed into the system from various building vibrations. A photograph of the entire test system is presented in figure 8.

B. Milling Yellow Dye Solutions

It has been noted previously[19, 20, 21, 22] that aqueous solutions of milling yellow dye having concentrations from 1.2 to 1.5% by weight are strongly birefringent. During the course of the investigations presented here, solutions from 1.20 to 1.90% have been used. It was noted that at a room temperature of 23° centigrade, a 1.90% solution becomes useless after an hour or so due to cloudiness and striations that become evident in the fluid. The fluid exhibits such strong scattering in this stage that it masks the birefringence completely.

Honeycutt and Peebles have measured the rheological properties of milling yellow solutions[21] and have found that the solutions exhibit non-Newtonian viscosities depending on concentration, temperature, and rate of shear. The solutions are relatively stable at room temperature, as long as they are not in contact with two dissimilar metals. If dissimilar metals are present, an electrolytic reaction takes place, causing a powdery suspension to form throughout the fluid.

FIGURE LEGEND

Figure 8. A photograph of the entire test system

A. Variable phasing synchronous trigger circuit
B. Ballantine Model 643 vacuum tube voltmeter
C. Hewlett-Packard Model 122-A dual trace oscilloscope
D. Gaertner travelling telescope
E. Analyzer
F. Test cell
G. Polarizer
H. Interference filter and lens
I. Adjustable slit
J. General Radio Type 1531A Strobotac
K. Photocell
L. Steel Mass
M. Geophone driver
N. Geophone velocity monitor

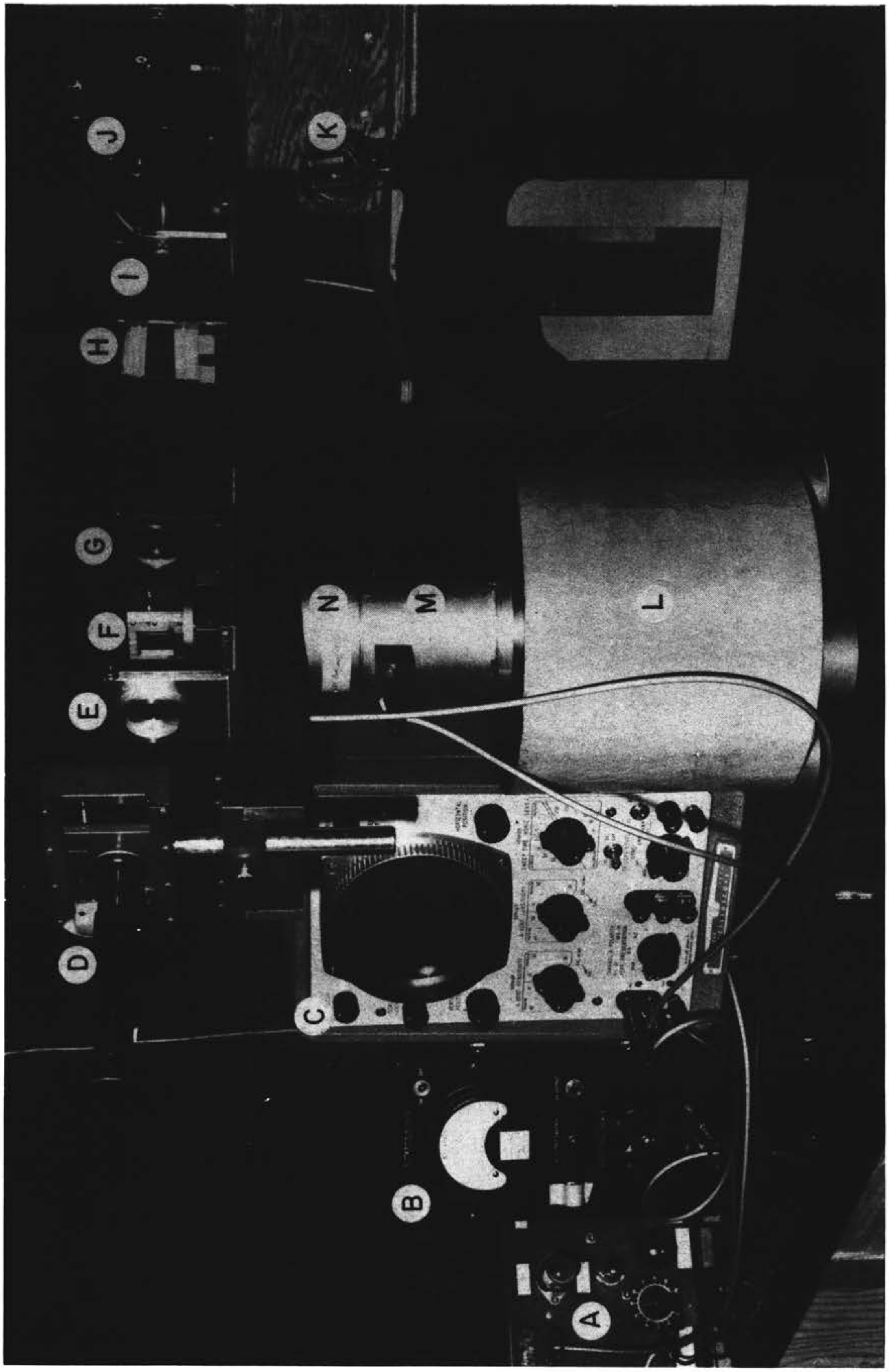

Figure 8

The milling yellow dye, although insoluble at room temperature, goes into solution quite readily when placed in gently boiling water. The solutions used for this investigation were all made by adding the proper amount of dye powder to gently boiling water, allowing the combination to boil gently for twenty minutes. The solution was then filtered immediately and set aside to allow it to cool to room temperature undisturbed.

The concentrations of the solutions used in these studies were determined by two methods. The first method used consisted of a determination based on the weight of the final solution and the weight of the powder added. The second method used was an evaporation method, in which a known weight of solution was placed in a weighing bottle and heated at about 90° centigrade for at least 12 hours, after which the residue was weighed. The concentration is then the ratio of the weight of the residue divided by the weight of the initial solution. Both methods have proved successful.

C. Description of the Experiment

The measurements were made as follows: first, using very low amplitude drive so that only zero order darkenings could occur, the phasing of the light pulse was varied until the zero order darkening occurred. Having once established the location of the zero order fringes for the given frequency and temperature, the phase was set so that the light flashed 90° earlier or later than the zero order phasing. Thus, the gap was illuminated at the time at which the fluid exhibited the greatest sensitivity, as is noted in the following chapter. The amplitude of the plane motion was increased then until the field went dark, corresponding to a retardation $|\delta| = \lambda$, the wavelength of the illuminating light. The velocity monitor output for this particular amplitude then was recorded. The amplitude could then be increased again, and retardation corresponding to several wavelengths would appear. The process could be repeated until the system could no longer provide enough drive to obtain more retardation.

Temperature runs were made by placing either a heat sink, in the form of an ice and water mixture, or a heat source, in the form of boiling water, in a metal container on top of the test cell. In either case the test cell and heat sink or source were allowed to reach an equilibrium temperature before the sink or source was removed. The temperature of the fluid in the gap was assumed to follow that of the brass cell quite closely, so the temperatures indicated in the figures are the temperatures of the brass cell itself, measured at an inside wall with a mercury thermometer.

Frequency runs were made by repeating the basic measurement procedure for many frequencies. The concentration studies were made by following the basic measurement procedure for many fluids. After a fluid had been examined, it was removed from the test cell by a hypodermic syringe and the cell flushed out with water, then dried as much as could be done easily. The gap was dried with strips of paper towelling. Then the new solution was added and the measurement repeated. Frequencies below 10 cps failed to trigger the Strobotac.

Extinction angle measurements were made by rotating the crossed polaroids until the field was dark irrespective of the phase setting. The angle between the vertical and the polaroid orientation is the extinction angle since the streamlines, being parallel to the plane, are vertical.

A Lucite reflector and a plane coated with polystyrene were also used to determine the effect, if any, of having conductors or non-conductors in contact with the fluid. No differences were detectable.

The next chapter presents the experimental results obtained by the procedures outlined in this chapter.

CHAPTER IV

EXPERIMENTAL RESULTS

A. The Fundamental Curve

The fundamental curve relating the mechanical and optical parameters for a 1.70% solution being sheared at 35 cps is presented in figure 9. The curve was obtained by noting the phasings at which $|\delta| = N\lambda$ for a given plane velocity, then changing the velocity and repeating the phase scan. The $\omega t = 0$ and $\omega t = 180$ degree points indicate the places where the plane velocity is a maximum. Hence, the minimum point of the curve, for which $\sec(\omega t + \theta_S) = 1$ is shifted to the left about 9 degrees from the point at which the displacement of the plane is maximum. This shift is the same shift exhibited by the zero order darkenings with reference to the $\omega t = 0$ and $\omega t = 180$ degree lines. For this reason the zero order darkening phasings can be used to determine the phasing of the minimum point of the curve. Note that the higher order effects as well as the zero order effects show no dispersion with amplitude of plane motion for a driving frequency of 35 cps and rms velocity gradients below 28 per second. If the measurements are made over wider ranges of ωt, the curves duplicate themselves, each 180-degree interval corresponding to all other 180-degree intervals. Knowing the manner in which the phase and magnitude of the minimum point of the curve varies as a function of various parameters permits one to calculate the variations in S and θ_S with these parameters. The following sections discuss such variations.

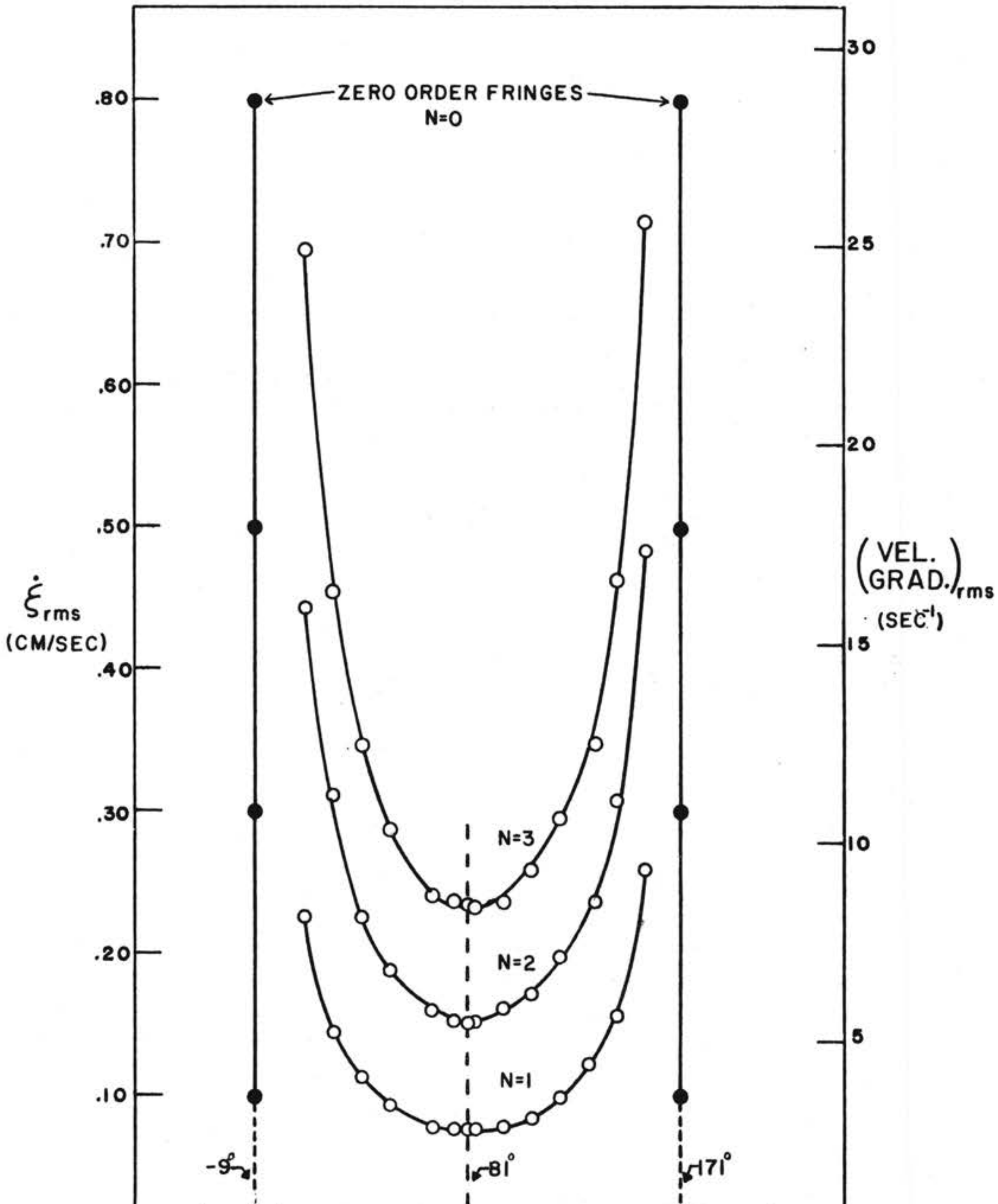

Figure 9. Plane velocity and velocity gradient versus phase of the plane motion for a 1.6% solution of milling yellow for which the driving frequency was 35 cps., and the room temperature was 23.0 degrees centigrade.

B. The Variation of S^* with Frequency

Figures 10 and 11 show the variations of S and θ_S as a function of frequency, where the values of θ_S are somewhat arbitrary, since θ_S is known only to within $\theta_S \pm \pi$. The values plotted were obtained for a 1.70% solution of milling yellow, at a temperature of 23.6° centigrade for an optical retardation δ . Note that the S versus frequency plot has a first power slope, indicating that the amplitude of plane motion required to cause one wavelength retardation is a constant over the frequency span covered. Beyond approximately 90 cycles per second the assumption that an approximately linear velocity gradient exists in the gap is probably in error, since the $\frac{\lambda}{D}$ ratio is less than 10 (See equation 2.17).

The θ_S curve for the same fluid indicates that the phasing of the optical effect is not a function of frequency for the frequencies at which measurements were made. Several concentrations have been tried, and none have ever shown any dependence of θ_S on frequency. However, it would seem that if the frequency span were made large enough some change should be detectable.

C. The Variation of S^* with Temperature

Figures 12 and 13 indicate the values of S and θ_S obtained for a 1.70% solution of milling yellow as a function of temperature for a driving frequency of 25 cps. Companion measurements of the complex viscosity of the same solution as obtained from studies of oscillation of the fluid in circular tubes showed that the rigidity of the fluid disappears at approximately 45° centigrade, the same temperature for which S would approach zero from an extrapolation of the S versus temperature curve. Readings could not be made for less than 8×10^{-10} seconds, since the system could not provide enough drive to obtain a

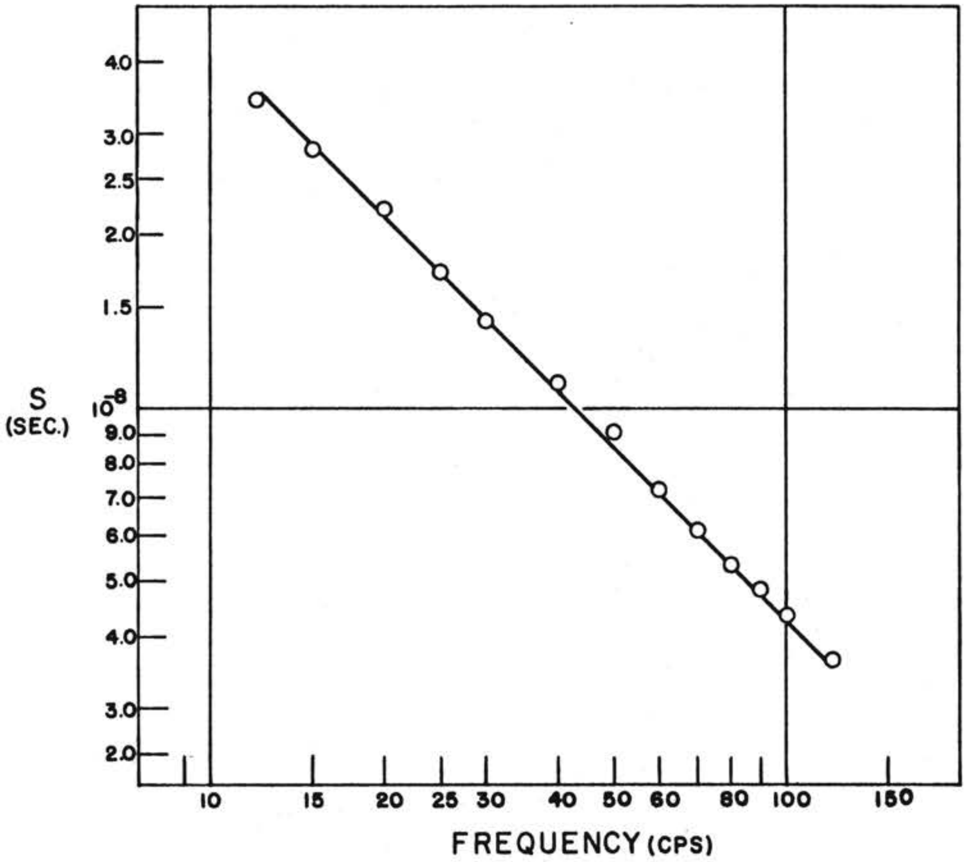

Figure 10. The magnitude of the complex optical coefficient versus frequency for a 1.72% solution of milling yellow. The room temperature varied from 20.8 degrees centigrade to 20.5 degrees centigrade during the measurements.

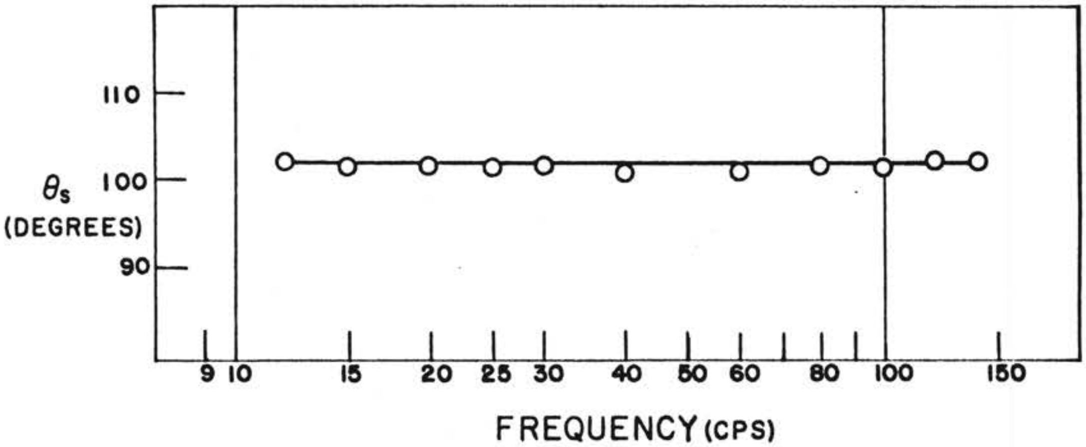

Figure 11. The phase angle of the complex optical coefficient versus frequency, for a 1.72% solution of milling yellow. The room temperature varied from 20.8 to 20.5 degrees centigrade during the measurements.

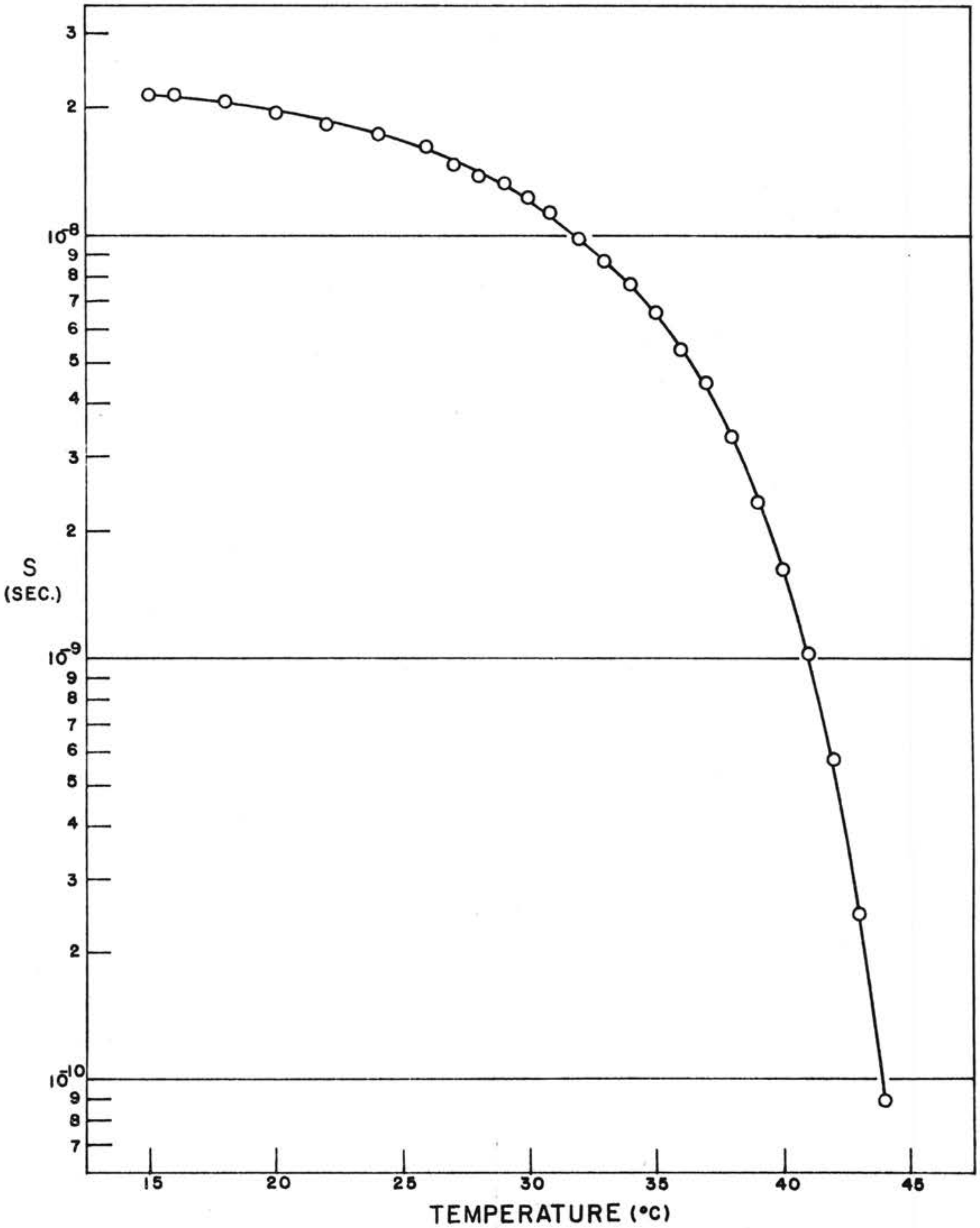

Figure 12. The magnitude of the complex optical coefficient versus temperature for a 1.72% solution of milling yellow. The driving frequency was 25 cps.

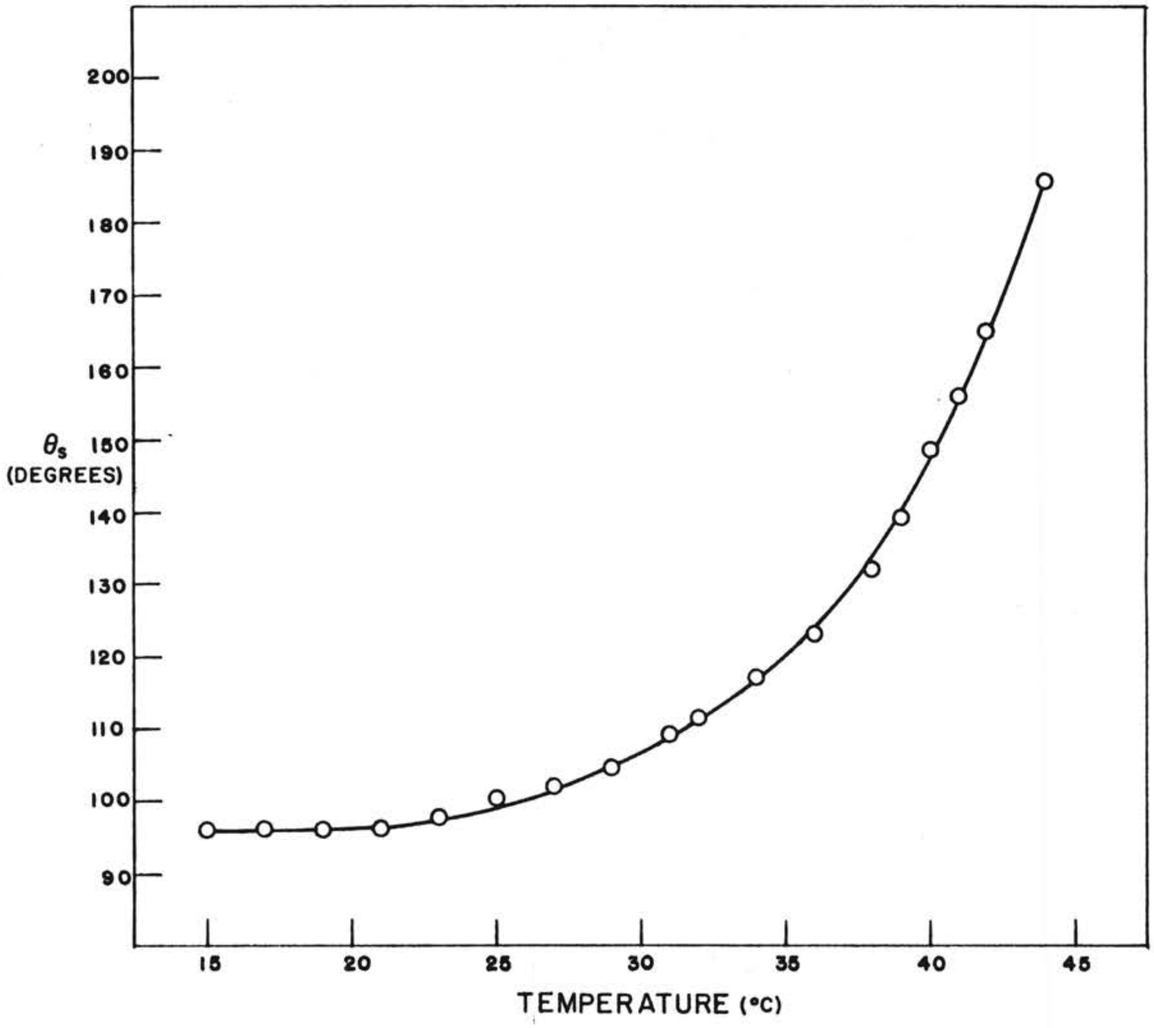

Figure 13. The phase angle of the complex optical coefficient versus temperature, for a 1.72% solution of milling yellow. The driving frequency was 25 cps.

full wavelength retardation below this point. No optical effect was observable for a temperature above 45° centigrade.

The plot of θ_S versus temperature shows the large phase changes that take place for temperatures approaching 45° centigrade. Note that θ_S has changed approximately 92 degrees, showing that at high temperatures the maximum optical retardation is almost in phase with the maximum velocity, instead of being within 7 degrees of the maximum displacement, as is the case below 18° centigrade. The low temperature measurements indicated that both S and θ_S reach constant values when the temperature reaches 17° centigrade. However, measurements could not be made below 15° centigrade due to striations of varying density and cloudiness that form in the fluid at that temperature. The striations caused an optical scattering that masked the birefringence entirely. The slight deviations on the S and θ_S versus temperature plots at a temperature of approximately 25° centigrade were probably due to the interchanging of the heating and cooling devices, since below 25° centigrade the test cell was cooled while above 25° centigrade it was heated.

D. The Variation of S^* with Concentration

Figures 14 and 15 present the values of S and θ_S obtained for solutions made from a 1.95% stock solution of milling yellow by dilution with distilled water. The measurements were made for a driving frequency of 25 cps. The base solution was diluted with the proper amount of water to give the desired concentration, and the diluted solutions were then brought to the boiling point, after which they were allowed to return to room temperature. All of the solutions were heated in the same water bath for the same length of time so that their relative concentrations

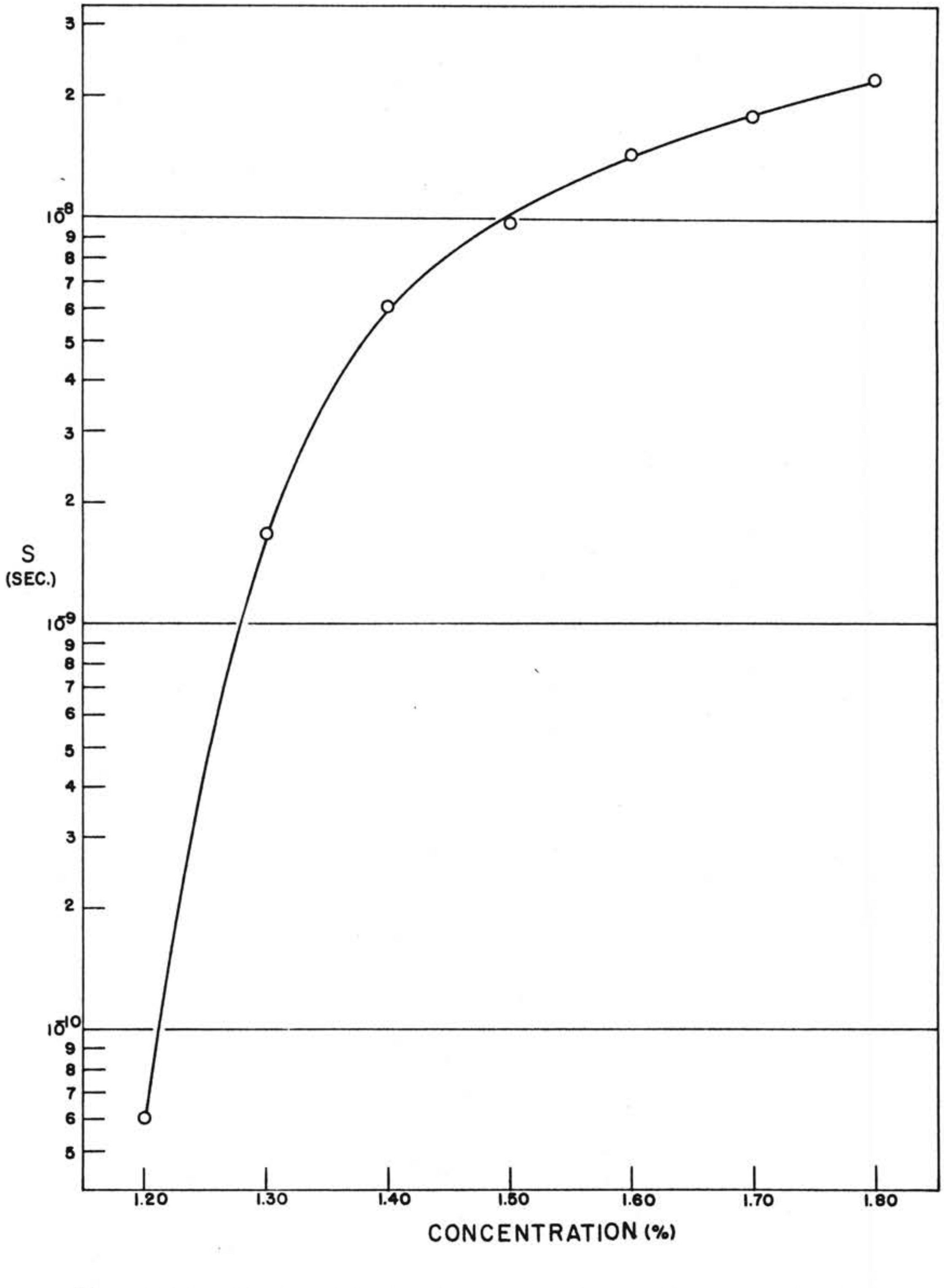

Figure 14. The magnitude of the complex optical coefficient versus concentration, for a driving frequency of 25 cps. The room temperature was 20.8 degrees centigrade.

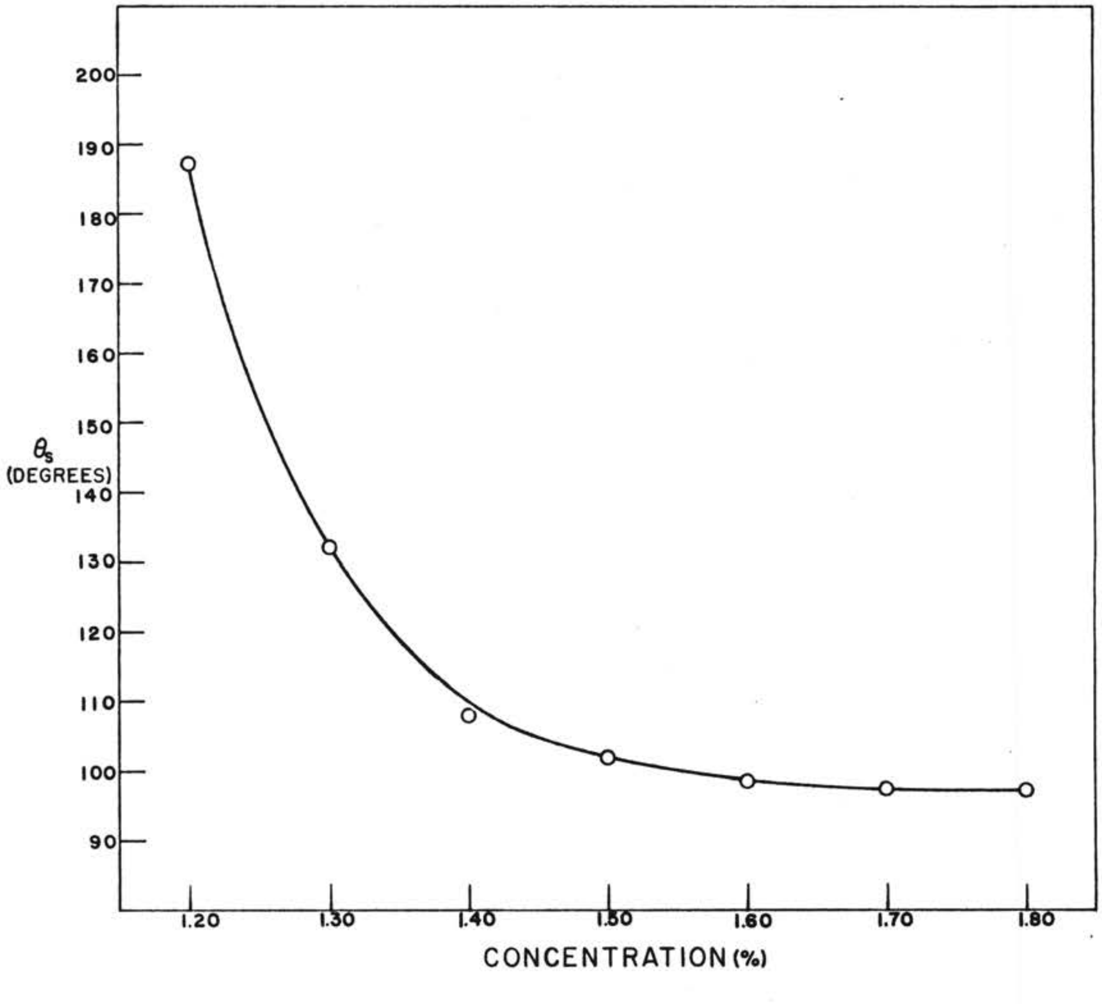

Figure 15. The phase angle of the complex optical coefficient versus concentration, for a driving frequency of 25 cps. The room temperature was 20.8 degrees centigrade.

would remain quite accurate, although their absolute concentrations might deviate slightly from the calculated values. The test cell temperature was 20.8° centigrade for these measurements. A very sharp decrease in σ is noted for a concentration close to 1.20%, and below 1.20% no measurements could be made because of insufficient drive. Again, companion measurements of the rigidity of the same solutions using the driving frequency of 25 cps showed that the rigidity of the solution was decreasing very rapidly in the same region, becoming immeasurable at 1.20%.

The θ_σ versus concentration curve shows a wide variation in θ_σ corresponding to a phase shift of approximately 90 degrees. For concentrations near 1.90% the solutions became striated and cloudy, similar to the striations appearing at low temperatures in the temperature study. Again the striations caused so much scattering that the birefringence was effectively masked.

E. The Variation of σ^* with Age of Solution

All of the measurements presented up to this point were made within 100 hours of the preparation of the 1.90% solution from which the test solutions were prepared, except for the data presented in figure 9. Hence, a study of the effect of aging of the solution was made, extending for 100 hours after the time at which the solution was prepared. The system temperature fluctuated, however, due to fluctuations in the room temperature. In figures 16 and 17 the values of σ and θ_σ as a function of time are presented for a 1.50% solution being sheared sinusoidally at 25 cps. The room temperature fluctuated 4° centigrade over the 100 hour period. Approximate corrections for the temperature changes are indicated by arrows. The corrected curves may show slight changes in σ

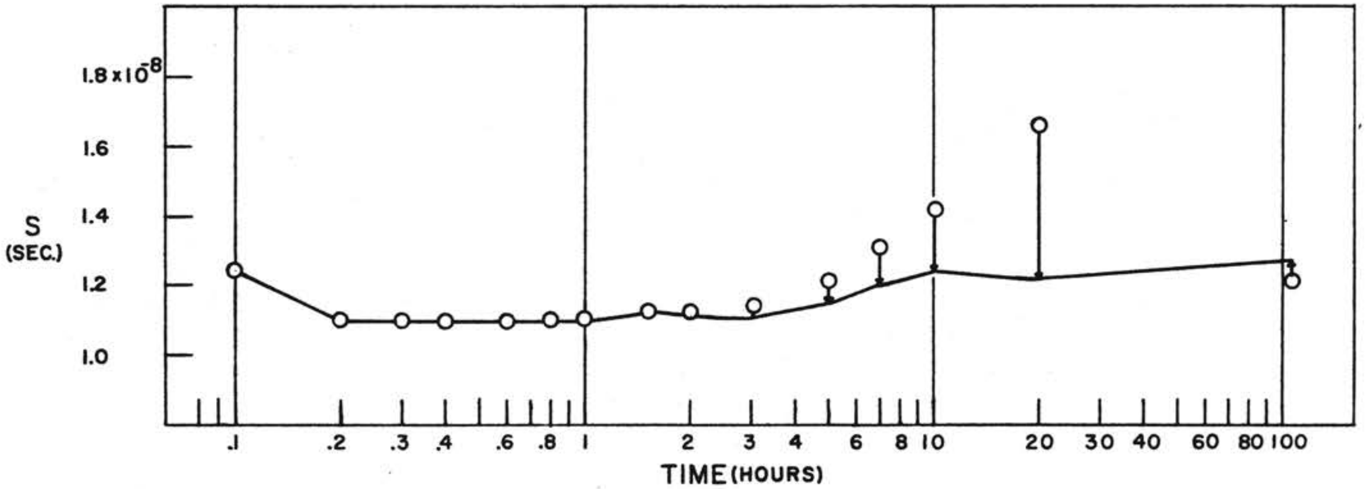

Figure 16. The magnitude of the complex optical coefficient versus time, for a 1.5% solution of milling yellow, using a driving frequency of 25 cps. The room temperature varied from 21.0 to 24.8 degrees centigrade over the time span indicated. The arrows drawn indicate approximate temperature corrections for temperatures differing from 24.2 degrees centigrade.

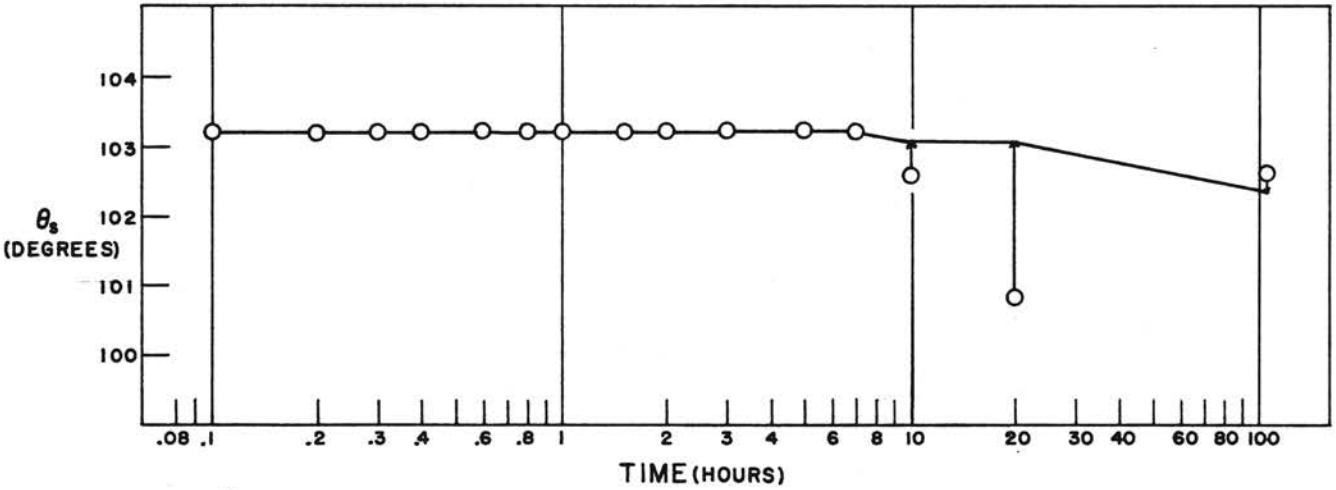

Figure 17. The phase angle of the complex optical coefficient versus time, for a 1.5% solution of milling yellow, using a driving frequency of 25 cps. The room temperature varied from 21.0 to 24.8 degrees centigrade over the time span indicated. The arrows drawn indicate approximate temperature corrections for temperatures differing from 24.2 degrees centigrade.

and θ_s with time, but the temperature fluctuations were large enough to make such a conclusion rather questionable. Certainly no large changes occurred in the first 100 hours. Three different concentrations were tested and all yielded similar results. These findings agree with the findings of Prados and Peebles[20], who noted that no changes due to aging could be detected for the first few weeks, although appreciable differences were present after six months.

F. The Variation of Extinction Angle

Extinction angle measurements have been made for several solutions of various concentrations using frequencies from 10 to 100 cps and amplitudes from the maximum obtainable to the minimum measurable. No variation of the extinction angle from 45^o and 135^o has ever been noted for any phasing during a given cycle.

CHAPTER V

DISCUSSION OF EXPERIMENTAL RESULTS AND SUGGESTIONS FOR FURTHER STUDY

A. Discussion of Experimental Results

The fundamental curve presented in figure 7 indicates that for rms velocity gradients less than 30 per second at a driving frequency of 25 cps the measurements for milling yellow solutions are not amplitude dependent. This is, the increase in velocity gradient necessary to provide a retardation of an additional wavelength is the same for rms velocity gradients up to 30 per second. This corresponds to the maximum velocity gradient obtainable by the system at present, since the geophone driving unit was not designed to allow larger excursions of the driving coils. The velocity gradients obtainable could be increased by decreasing the gap width, but the optical system in use at present will not allow one to work with gap widths of less than 5 mils. Hence, the upper limit for rms velocity gradients obtainable from the system would be on the order of 60 per second. Note that steady flow measurements are made using velocity gradients up to one hundred per second for liquid suspensions, and up to several thousand per second for pure fluids. Hence, for the apparatus discussed here one would be limited to measurements of fluids which exhibit high optical sensitivities like vanadium pentoxide and milling yellow, since retardations of an integral number of wavelengths must be obtainable at low velocity gradients. All of the measurements are reproducible to within 3%, the reproducibility being limited by the oscilloscope face readings. Some error in the value of S is introduced by neglecting end corrections for the plane, but these corrections are probably not large.

The mechano-optic relation presented in Chapter II was

$$\Delta n = S^{*} \frac{\partial \dot{\xi}}{\partial x} \tag{5.1}$$

In the experiments mentioned in Chapter I all the work was done in steady flow--constant shear rate--after equilibrium had been established. Thus the optical constants and extinction angles measured were characteristic of an equilibrium situation. In the work presented here, however, the plane velocity is a sinusoidal function of time. Hence, depending on the time required for a given fluid to reach equilibrium, the values of the extinction angle and the optical constant might or might not be the same as the steady flow values. Therefore, unless one knew the time required for a given fluid to reach an equilibrium state, it would be very difficult to make any kind of comparison between the steady flow and the time-varying flow situations. For example, would the fluids that exhibit a change in extinction angle with shear rate be expected to exhibit a similar change in the non-equilibrium study? Because of these complicating factors, no attempt has been made here to correlate the steady state work with the dynamic state work presented here, other than to note that the value of Δn measured here agrees with the values obtained by Honeycutt and Peebles in steady flow (See Table 1).

The apparent relation between the disappearance of the birefringence and the disappearance of the rigidity of the fluid was pointed out in the

TABLE I

COMPARISON OF THE DIFFERENCE IN INDICES OF REFRACTION FOR CORRESPONDING LEVELS OF STRESS FOR SEVERAL SUBSTANCES

Fluid	Δn	Ref. List Number
Milling yellow solution, steady flow	10^{-5}	19
Milling yellow, sinusoidal motion	10^{-5}	
Glasses, static stress	10^{-14}	12
Celluloid and Bakelite, static stress	10^{-10} to 10^{-12}	12
Pure liquids, steady flow	10^{-10} to 10^{-12}	19
Vanadium Pentoxide, steady flow	10^{-4}	19
Polystyrene in Toluene	10^{-7}	6
Cellulose acetate in cyclohexanone	10^{-7}	6
Nitrocellulose NC2	10^{-7}	6

last chapter. The fact that θ_S changes so much with temperature and concentration seems to indicate that the relation between mechanical and optical properties is quite complex and not so simple as would seem to be indicated by the corresponding decreases in S and the fluid rigidity. More work will have to be done before much can be said about the apparent mechano-optic relation.

From figures 10, 11, 12 and 13, one can see that the temperature and concentration curves are similar if one reverses the temperature scales, the agreement being better for the S curves than for the θ_S curves. Thus, a high temperature corresponds to a low concentration, and a low temperature corresponds to a high concentration.

An attempt was made to reduce the data to some expression showing the equivalence of changes in S^* for temperature, concentration and frequency. However, the temperature and concentration curves differed enough in shape to make such a reduction impossible, apparently. It is possible that the experimental errors in measuring temperature might have caused such a deviation, since the temperature of the cell was measured, and not the temperature of either the reflector surface or the fluid in the gap.

B. Conclusions

On the basis of the work presented here it would appear that the test system described is adequate for measurements of the complex optical factor S^* for fluids exhibiting retardations of at least one wavelength at rms velocity gradients below 30 per second for driving frequencies down to 10 cps. However, no previous measurements have been located, so no independent confirmation is available.

The mechano-optic relation proposed in equation 2.15 is a convenient means of displaying the variation in both amplitude and phasing of the optical retardation of the fluids as revealed by the measurements made using the test apparatus.

The measurements made using the aqueous milling yellow solutions indicate that the magnitude of S^* and the rigidity of the fluid are related, although the relation is undoubtedly complex as is indicated by the large variations in θ_S with temperature and concentration. However, the magnitude of S^* seems to decrease rapidly when the fluid rigidity also decreases rapidly.

C. Suggestions for Further Study

Extensions of the experimental work presented here will be necessary before a universal mechano-optic relation for birefringent media can be developed. First, frequency studies should be extended to low frequencies, on the order of .1 cycle per second at least, to determine any change in the S and θ_S that might take place. Since the fluids are not birefringent under static pressures, some changes in S^* should present themselves as the frequency is decreased. Second, since all the work presented here was done using a monochromatic light source of wavelength 5780 Angstroms, a study to determine the variation of the complex optical coefficient S^* as a function of the wavelength of the light passing through the fluid would be of value, especially since the static transmission curve for milling yellow shows very marked maxima and minima for wavelengths from 8000 Angstroms to 13,000 Angstroms. Studies using wavelengths in this region might indicate something about the structure of the milling yellow solutions. Third, an optical compensator--perhaps of the Babinet type--to measure small retardations should be added to the system to allow one to make measurements on fluids of lower sensitivity, so that more fluids of various types could be studied. Fourth, independent confirmation of these measurements should be sought.

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