

# Magnetic Double Refraction in Liquids

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An apparatus for measuring magnetic double refraction (Cotton-Mouton effect) in liquids is described. The chief feature of the apparatus is a very sensitive variable order compensator which is discussed in detail. Measurements made with this instrument indicate that path differences as small as  $3 \times 10^{-5} \lambda$  can be determined with a precision of about 12 percent provided use is made of very intense light having a wave-length lying within the region which corresponds to maximum visual response. The Cotton-Mouton constants of water and several organic liquids of the aliphatic series including four normal alcohols and five normal acetates are reported and compared with the previous determinations made by other investigators. Certain discrepancies are noted and discussed.

## I. INTRODUCTION

IN 1907 Cotton and Mouton<sup>1</sup> discovered that certain isotropic organic liquids when placed in a strong transverse magnetic field acquire the doubly-refracting property of a uniaxial crystal with the optic axis in the direction of the field ( $H$ ). Thus if a plane-polarized beam of light with a ray direction perpendicular to  $H$  is incident on such a liquid, the light will in general be transmitted through it as two component waves with the electric field in one wave vibrating in a plane parallel to  $H$  and the electric field in the other in a plane perpendicular to  $H$ . If  $n_p$  and  $n_s$  denote, respectively, the indices of refraction for these two waves, a simple calculation shows that they will emerge with a path difference  $\Delta$  (expressed in number of wave-lengths):

$$\Delta = L(n_p - n_s)/\lambda, \quad (1)$$

where  $L$  is the length of the specimen in the field  $H$  and  $\lambda$  is the wave-length of the light in vacuum. As path differences so produced are small, the emergent light will be characterized by a weak elliptic polarization and the experimental problem in researches on the "Cotton-Mouton effect" therefore consists essentially of an accurate measurement of this elliptic polarization.

The relation between the variables  $\Delta$ ,  $L$  and  $H$  was found by experiment<sup>2</sup> to be:

$$\Delta = C_m L H^2, \quad (2)$$

" $C_m$ " being a proportionality factor which is now

usually referred to as the "Cotton-Mouton constant." This constant is different for different substances, being positive in some and negative in others; it also varies with their temperature and the wave-length of the incident light.<sup>3</sup>

The classical theory of magnetic (and electric) double refraction developed by Langevin and Born<sup>4</sup> accounts for these relationships on the basis of anisotropic electric and magnetic polarizabilities of molecules. While this theory is strictly applicable only in the case of gases, such experiments in magnetic double refraction have hitherto presented almost insuperable difficulties and the theory has therefore been applied to liquids only, where in most instances it has been found to predict approximately the experimental results.<sup>5</sup> The new quantum mechanics has yielded little more than the classical theory.<sup>5</sup>

As Raman<sup>6</sup> has pointed out, the importance of magnetic double refraction measurements from the standpoint of the general theory of magnetism is due to the use that can be made of Cotton-Mouton constants in evaluating the magnetic anisotropy of molecules. Suggestive attempts in this direction have been made by Ramanadham<sup>7</sup> and Chinchalkar<sup>8</sup> for the simpler organic molecules of the aliphatic series by means of the Langevin-Born theory. As the value of  $C_m$  is generally very small in aliphatic liquids,

<sup>3</sup> For a general resumé and complete references see Beams, *Rev. Mod. Phys.* **4**, 160-172 (1932).

<sup>4</sup> See Debye, *Marx Handbuch der Radiologie* **6**, 754-769, Leipzig (1925).

<sup>5</sup> Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford Univ. Press (1932), p. 367 para. 84.

<sup>6</sup> Raman, *Phys. Soc. Proc.* **42**, 309 (1929).

<sup>7</sup> Ramanadham, *Ind. J. Phys.* **4**, 15 (1929-30).

<sup>8</sup> Chinchalkar, *Ind. J. Phys.* **6**, 165 (1931).

<sup>1</sup> Cotton and Mouton, *C.R.* **145**, 870 (1907).

<sup>2</sup> Cotton and Mouton, *J. de Physique* **1**, 16 (1911).

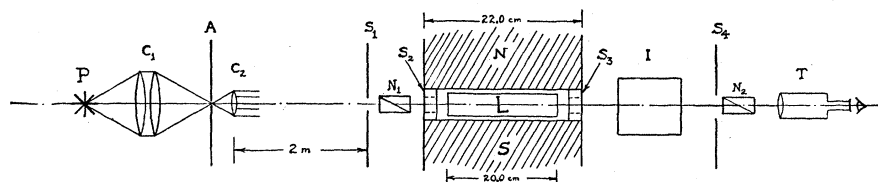


FIG. 1. Schematic diagram of the apparatus.

an apparatus of high sensitivity is needed for precise measurements. It is the purpose of this paper to describe such an apparatus and to present the results which have been obtained with it.

## II. APPARATUS AND PROCEDURE

A schematic diagram of the apparatus is given in Fig. 1:  $P$  is a 110 watt Pointolite lamp;  $C_1$  is the condenser arranged to focus the bright bead in the lamp upon a circular aperture of 1 mm diameter in the screen  $A$ . This aperture acts as a "point" source of light for an achromatic collimating lens  $C_2$ .  $S_1$  and  $S_4$  are the mountings for the polarizing and analyzing prisms,  $N_1$  and  $N_2$ , a combination discussed later in more detail.  $S_2$  and  $S_3$  are brass blocks, 6.10 mm wide, pierced along the axial line of the optical system with holes 5 mm in diameter; these blocks serve both as spacers for the pole-pieces  $N$  and  $S$  of the magnet and as diaphragms in the optical system. Under these conditions the light passing through the specimen tube  $L$  is parallel to at least  $0.8^\circ$ .

Failure to secure parallelism of the beam or to align it in a direction perpendicular to  $H$  results in the appearance of the Faraday effect, which acts to reduce the sensitivity of the apparatus. A convenient test of the fulfillment of these two conditions consists in placing carbon tetrachloride in the specimen tube, whereupon, if the lens system is properly adjusted, application or removal of the magnetic field will produce no noticeable optical effect since this substance shows no magnetic double refraction. Parasitic reflection of light in the system, which also reduces the sensitivity, was practically eliminated by using copper specimen tubes the walls of which were exposed to moist hydrogen sulfide, thus giving them a low reflecting power surface and also leaving them chemically inert. The tubes were 20.0 cm long with a rectangular cross-

section 12 mm high and 6 mm wide with a square aperture 6 mm high and 5 mm wide sealed with carefully annealed microscope cover glass.

The cements suggested by previous investigators in this field for pasting the glass to the metal tube were found to be unsuitable as they dried hard and caused strains to be set up in the glass, resulting in a troublesome residual double refraction. To avoid this effect, very viscous and non-drying cements were used. In experiments on the alcohols a small amount of Merck's anhydrous lanolin was melted and titrated through a large amount of the alcohol to be examined. After repeated heating and stirring the insoluble part was recovered and the titration process repeated. The remaining insoluble part constituted a satisfactory cement. For the acetates the cement consisted of a mixture of dextrin, dextro-mannitol and glycerine treated with the respective acetates in a similar manner. It was found important to have the end glasses perpendicular to the axis of the tube and for this reason very thin layers of cement were used.

In Fig. 1,  $S_1$  and  $S_4$  represent twelve inch circular duraluminum disks graduated in quarter degrees; by means of verniers these circles could be read to  $0.01^\circ$  directly. The maximum error of graduation of the circles was found not to exceed the width of the ruling at any position and was thus estimated to be not greater than  $30''$  of arc. Both circles carried polarizing prisms,  $N_1$  and  $N_2$ , of the Glan-Thompson type with square end faces 12 mm on a side. These prisms have two distinct advantages over the usual type of nicol: (1) they give more nearly plane-polarized light, (2) when turned they do not cause the usual rotational displacement of the light beam. With the optical system diaphragmed as described Landolt's fringe is not visible when the nicols are crossed, indicating that the light traversing

the specimen is plane-polarized and of a single azimuth.

The pole pieces *N* and *S* were specially designed for this investigation; their construction is indicated by an end section shown in Fig. 2. The high permeability of the "Weiss" iron insert allows higher field strengths to be obtained than would be the case if the pole pieces were constructed entirely of Swedish iron. With the magnet coils connected in parallel a total exciting current of 26 amp. was found to produce an average field of 22,600 gauss. The field strength was measured by suspending a current element in the gap and measuring the pull on the element by means of a balance. By mounting the balance on tracks above the magnet it was possible to make a point to point plot of the field. The error in measuring *H* was estimated to be less than 2 percent.

The instrument *I* in Fig. 1 represents the compensator used to measure the double refraction. It is of the "variable order" type and was first described by Palmer.<sup>9</sup> It consists essentially of three strain-free pieces of microscope cover glass arranged as shown in Fig. 3. The two horizontal strips are 25 mm long, 5 mm wide and about 0.2 mm thick. The lower, hereafter designated the "half-shade," may be subjected to pure tensile stress in a horizontal direction by the arrangement shown in the figure. The upper glass is kept strain-free and can be adjusted to lie in a plane which is parallel and adjacent to that of the half-shade. If the contiguous edges of the two strips have been ground and polished

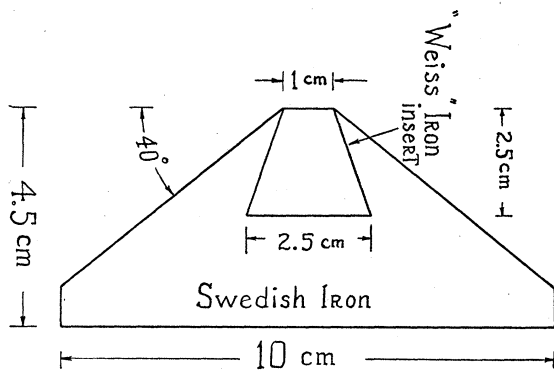


FIG. 2. End section of pole pieces.

<sup>9</sup> Palmer, Phys. Rev. 17, 409 (1921).

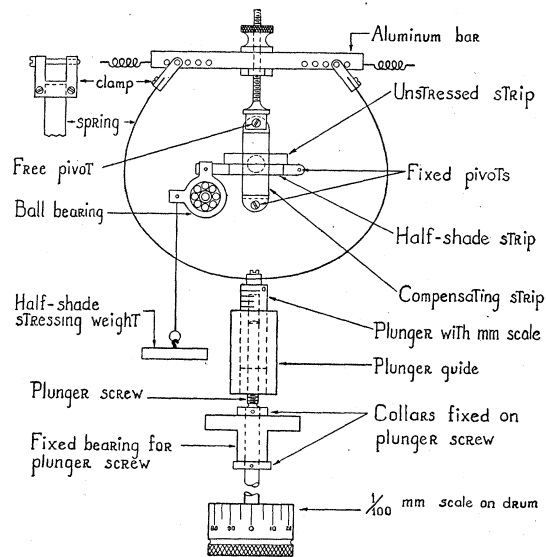


FIG. 3. Arrangement of microscope cover glasses.

to an optical flat and are not chipped, the dividing line between the two halves of the field of view (indicated by the dashed circle in Fig. 3) can be made, by careful adjustment, to vanish almost completely when the intensity of light in both is the same. In making observations the strips are viewed through the short-focus, low-power observing telescope *T* (Fig. 1) which is focussed upon their edges. The third glass of the same length and thickness as the horizontal ones, but 12 mm wide, is mounted behind them and covers the whole field of view. This strip, hereafter called the "compensating" strip, can be given pure tensile stress in the vertical direction by means of the indicated flat steel spring.

Since glass under tension behaves as a positive uniaxial crystal with the optic axis in the direction of the applied stress, the half-shade and compensating plates are therefore equivalent to crossed positive doubly-refracting plates of variable thickness. Photoelastic investigations have shown that the relation between the tensile stress applied to a glass plate and the resulting double refraction is linear,<sup>10</sup> hence:

$$n_e - n_0 = KT. \quad (3)$$

<sup>10</sup> Coker and Filon, *Photoelasticity*, Cambridge Univ. Press, 1931, p. 185, para. 3.03.

In this relation  $n_e$  and  $n_o$  are the "extraordinary" and "ordinary" indices, respectively, and  $T$  is the applied stress. The proportionality factor  $K$  depends upon the composition of the glass, wave-length of light, and temperature (a point which will be considered later). With the aid of Eqs. (1) and (3) a quantity  $\delta$  known as the "order" of a birefringent plate can be expressed as follows:

$$\delta \equiv 2\pi\Delta = 2\pi L(n_p - n_o)/\lambda = K'T. \quad (4)$$

Eq. (4) has been verified by Palmer<sup>9</sup> for microscope cover glass.

From the usual theory of double refraction it follows that if two birefringent plates with "fast" axes at right angles are placed between a polarizing and analyzing nicol the intensity  $I$  of the light wave leaving the analyzer can be expressed as follows:

$$I = \frac{1}{2}A^2[\cos^2 \theta + \sin 2\rho \sin 2(\theta - \rho) \sin^2 (\delta_1 - \delta_2)/2], \quad (5)$$

where  $A$  is the amplitude of the electric vector in the plane-polarized wave leaving the polarizer,  $\theta$  is the angle between the transmission azimuth of the analyzer and the transmission azimuth of the polarizer (the latter serving as a convenient fiducial azimuth from which all angles are measured),  $\rho$  is the angle which locates the azimuth of the "fast" axis of the compensator plate, and  $\delta_1$  and  $\delta_2$  represent the "order" of the half-shade and compensator plates, respectively. Eq. (5) serves to define the intensity of light in the lower half of the field of view (as shown in Fig. 3) and will be denoted by  $I_1$ . Since there is only one birefringent plate in the upper half of the field of view, the corresponding intensity  $I_2$  is expressed by:

$$I_2 = \frac{1}{2}A^2[\cos^2 \theta + \sin 2\rho \sin 2(\theta - \rho) \sin^2 \delta_2/2]. \quad (6)$$

$I_1$  and  $I_2$  are evidently equal when:

$$\delta_1 = 2\delta_2. \quad (7)$$

From Eqs. (1) and (4) the condition for a matched field may also be written:

$$T_1 = 2T_2. \quad (8)$$

To measure the order  $\delta_3$  of a third doubly-refracting medium introduced into the optical

system, e.g. (the double refraction of a liquid brought about by the action of the magnetic field), the simplest procedure is, perhaps, to orientate its optic axis so as to coincide with that of the half-shade plate. Since the optic axis of the liquid in magnetic birefringence is coincident in direction with  $H$ , and  $H$  and  $T_1$  are both horizontal, this condition is already fulfilled. Thus, if a liquid shows *positive* double refraction of order  $\delta_3$ , the effect in the compensator is exactly the same as an increase in  $T_1$ , for now  $\delta_3$  and  $\delta_1$  are both appropriate to positive plates of the same azimuth. If  $\delta_1$  is kept fixed, Eqs. (5) and (6) show that the match of the half-shade field will be restored when:

$$\delta_1 + \delta_3 - \delta_2' = \delta_2' - \delta_3, \quad \therefore \delta_1 = 2(\delta_2' - \delta_3). \quad (9)$$

From Eq. (7) it therefore follows that  $\delta_2' > \delta_2$ , or from Eq. (8) that  $T_2' > T_2$ .

Similarly for *negative* double refraction;

$$\delta_1 = 2(\delta_2' + \delta_3), \quad (10)$$

with  $\delta_2' < \delta_2$  and  $T_2' < T_2$ .

From Eqs. (4), (7) and (9):

$$\delta_3 = K' \cdot \Delta T_2 \quad (11)$$

where  $\Delta T_2 = (T_2' - T_2)$ . Eq. (11) provides a convenient criterion for both the sign and the magnitude of the double refraction of the liquid under investigation.

In terms of the physical adjustment of the compensator,  $T_1$  being kept fixed, Eq. (11) shows that if after application of the magnetic field it is necessary to increase the tension on the compensating strip to restore the balance of the optical field then the liquid exhibits positive double refraction; negative double refraction requires the tension to be decreased if the match is to be restored.

It is important to note that Eq. (11) is true whether or not the nicols are crossed. Reference to Eqs. (5) and (6) for  $I_1$  and  $I_2$  shows that if they were originally equal then any change in  $\theta$  will not destroy this equality. From this fact it follows that the appearance of the Faraday effect will not act to unbalance the optical field, and will not therefore be interpreted as a double refraction.

To define a measure of the sensitivity of the compensator let us suppose that the compen-

sating strip is given an increment of double refraction  $\Delta\delta_2$  over and above the double refraction  $\delta_2$  corresponding to some match point. The absolute change in intensity in the upper half of the field, owing to this increment, is expressed by:

$$\Delta I_2 = (\partial I_2 / \partial \delta_2)_{\text{match}} \cdot \Delta \delta_2, \quad (12)$$

and the corresponding change in intensity in the lower half by:

$$\Delta I_1 = (\partial I_1 / \partial \delta_2)_{\text{match}} \cdot \Delta \delta_2. \quad (13)$$

Account must be taken of the response characteristics of the eye, hence an appropriate definition of the sensitivity  $S$  is:

$$S = |\Delta I_2 / I_2 - \Delta I_1 / I_1|, \quad (14)$$

which in virtue of Eqs. (12) and (13) may be written:

$$S = \left| \left( \frac{\partial I_2 / \partial \delta_2 - \partial I_1 / \partial \delta_2}{I_2} \right)_{\text{match}} \cdot \Delta \delta_2 \right|$$

provided  $\Delta\delta_2$  is considered very small. With the aid of Eqs. (5) and (6) it follows that:

$$S = \left| \frac{\sin 2\rho \sin 2(\theta - \rho) \sin \delta_2}{\cos^2 \theta + \sin 2\rho \sin 2(\theta - \rho) \sin^2 \delta_2 / 2} \cdot \Delta \delta_2 \right|. \quad (15)$$

Excluding the values  $\theta = 0$ ,  $\rho = 0$ , the variables  $\theta$ ,  $\rho$  and  $\delta$  are all independent and the condition that each must satisfy in order that  $S$  shall be a maximum may be found in the usual way by setting:

$$\partial S / \partial \theta = 0, \quad \partial S / \partial \rho = 0, \quad \partial S / \partial \delta = 0.$$

These conditions are satisfied for:

$$\theta = \pi/2, \quad \rho = \pi/4, \quad \delta_2 = 0. \quad (16)$$

Hence, for maximum sensitivity the nicols should be crossed, the light vector should make an angle of  $45^\circ$  with the fast axis of the compensating plate, and the tension *on the half-shade* should be as small as is consistent with the desired range of the instrument. It should be noted that under these conditions the intensity of light in the half-shade field will appear quite low and the best results can therefore be obtained only when the observer's eye is dark-adapted.

As the above sensitivity analysis shows that the maximum rate of change of intensity of the

half-shade field with double refraction of the glass strips is secured when the light vector makes an angle of  $45^\circ$  with the axes of the strips; it therefore follows that, since the axes of the liquid coincide with those of the strips, the rate of change of intensity in the compensator with double refraction induced in the liquid will also be a maximum for the same orientation of the light vector. To secure this  $45^\circ$  setting, the direction of  $H$  was determined by placing a liquid of relatively large double refraction (nitrobenzene) in the tube, and moving the transmission azimuth of the polarizer slowly through the horizontal direction, the compensator having been rotated through  $45^\circ$  to preserve its sensitivity. Under these conditions the disappearance of double refraction signalizes the coincidence in direction of the light vector and the magnetic force  $H$ . This coincidence could be determined to within  $\pm 1'$  of arc.

The method of determining  $\delta_3$  was a comparative one and was based upon the magnetic double refraction of acetone as a standard. The procedure consisted in applying a given stress to the half-shade strip by hanging a weight on the stressing mechanism shown in Fig. 3. With the light beam traversing the specimen whose birefringence was to be measured, the corresponding reading of the deflection of the compensator spring was then observed when the optical field was matched. With a given weight on the half-shade six to nine readings were taken to determine this match point. This procedure was repeated with about four or five different weights, usually 20, 50, 70, 100 and 150 grams. The match points were then plotted as shown in Fig. 4, and double refractions determined by means of Eq. (11) in conjunction with this "calibration" curve. If, for instance, acetone were placed in the specimen tube and the field matched with 50 grams on the half-shade, application of the magnetic field would destroy this match. In order to rematch the optical field, it was found necessary to increase the tension on the compensating strip until the spring deflection reading was about 710. Referring to the calibration curve this reading will be seen to correspond to about 123 grams; application of the magnetic field therefore produces a double refraction in acetone which is the same as that

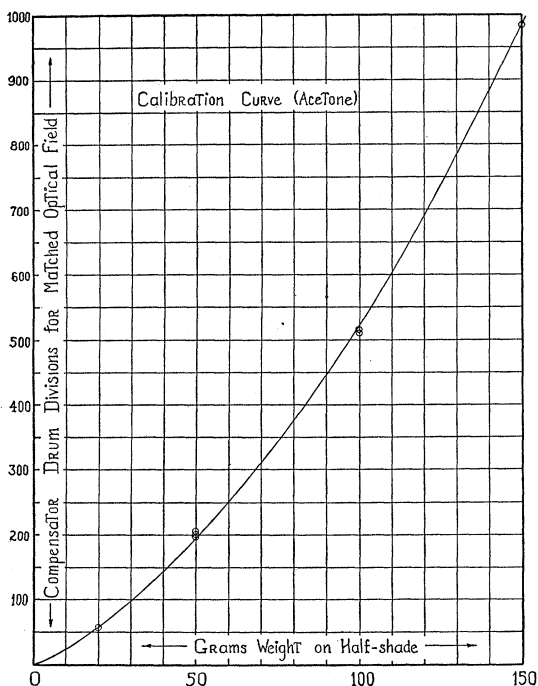


FIG. 4. Calibration curve of acetone.

produced by the application of an additional weight of 73 grams to the half-shade straining mechanism. If methyl acetate were placed in the tube, all other conditions remaining the same, the result found in this way would correspond to an increase of about 37.4 grams. If these increments are taken as a measure of the change in tension on the compensating strip, and are represented as  $\Delta T_2$  and  $\Delta T_2'$ , we may write:

$$\Delta T_2 / \Delta T_2' = C_m / C_m' \quad (17)$$

in virtue of the definition of order and Eqs. (2) and (11). It is usual to compare the double refraction of a given liquid with that of nitrobenzene under the same conditions, the latter being arbitrarily chosen to have a constant of 100. Cotton and Mouton<sup>11</sup> have found that on this scale acetone has a constant of 1.6. From Eq. (17) the relative constant of methyl acetate would therefore be:

$$C_m / 1.6(0) = 37.4 / 73.0, \quad C_m = 0.82.$$

As it was necessary to increase the tension  $T_2$  to rematch the optical field in both cases, Eq. (11)

<sup>11</sup> Cotton and Mouton, *Ann. de Chem. et Phys.* **28**, 236 (1913).

indicates that the sign of the constants is positive.

Early experiments carried out with a glass straining system similar to that described by Palmer<sup>9</sup> showed that the calibration curves were not reproducible. The match points were found to be exceedingly unstable; overnight shifts of 200 drum divisions often occurred even though the tension on the strips had been completely relieved. Attempts to eliminate this difficulty by making the stressing systems as frictionless as possible led to the arrangement shown in Fig. 3. Although these efforts resulted in some improvement, the fundamental trouble was not located until a careful investigation disclosed that the instability of the calibration was due to the effects of small temperature fluctuations upon the compensator, a change of 3°C accounting for a shift in the match points of about 200 drum divisions. From the reported temperature coefficients<sup>12</sup> of  $K$  in Eq. (3) it appears that changes of this magnitude are too large to be attributed to variations in the birefringence of strained glass with temperature; whether or not the effect is only incidental to the stressing systems employed is not known. When the compensator was placed in a constant temperature housing in which the fluctuations were less than 0.1°C, the calibration curves were found to be reproducible within the experimental error of the determination of the match points, which seldom exceeded 10 drum divisions.

The accuracy of determinations of Cotton-Mouton constants by the comparative method described above is obviously dependent upon the purity of the calibrating substance (acetone). Specimens of acetone from three different sources were therefore checked against each other. Sample (1) was Merck's "Reagent," (2) Baker Chemical Company's "Analyzed," (3) a sample of exceptional purity obtained through the kindness of Professor L. P. Hammett of the Chemistry Department of Columbia University. This sample was purified by refluxing the liquid over solid calcium oxide and solid potassium permanganate for about five hours to dehydrate it and oxidize the organic impurities that might be present; it was then carefully distilled.

<sup>12</sup> Coker and Filon, *Photoelasticity*, Cambridge Univ. Press, 1931, p. 243, para. 3.26.

The values of  $\Delta T_2$  obtained from these three samples were found to be, respectively: (1)  $72.8 \pm 1.0$  grams, (2)  $74.1 \pm 0.4$  grams, (3)  $72.8 \pm 0.9$  grams. Each of the above values is the average of four or more separate determinations and each single determination represents a mean of from five to nine readings with the magnetic field applied. The maximum deviation of any single determination from the mean of its set was 1.5 grams, and the average deviation of the single determinations is represented above as the precision measure of the set. The same statements, with the exception of the deviation of single determinations, apply to the values of  $\Delta T_2$  given in column (3) of Table II. As no special treatment was given samples (1) and (2), the final result for acetone was taken as:

$$\Delta T_2 = 72.8 \pm 1.0 \text{ grams.}$$

As a further check on this standard the constants of chloroform, ethylene dichloride and nitromethane were determined relative to acetone and then compared with those published by Cotton and Mouton<sup>11</sup> who used an absolute method. Because of its high sensitivity the range of the compensator was too small to measure the double refraction of these substances when contained in a 20.0 cm tube, hence for this comparison a shorter tube (length 7.04 cm) was substituted. The chloroform and ethylene dichloride were obtained from Eimer and Amend; the former liquid was of "tested purity" and carried an analysis; the latter was twice distilled before being used. The nitromethane was purchased from the Eastman Kodak Company (designated by E. K. C. in column 9, Table II) and was specified to have a boiling point between 98 and 101°C. The results are listed in Table I.

The above values of  $C_m$  given by Cotton and Mouton were calculated from measurements made with approximately monochromatic light

of mean wave-length  $\lambda = 578 \text{ m}\mu$  (yellow lines of the mercury arc). Preliminary experiments with the above-described compensator showed that high sensitivity could not be obtained with the monochromatic sources available or by the use of filters owing to their high absorption. By using the unmodified radiation from the Pointolite lamp under the condition corresponding to maximum sensitivity of the compensator (low intensity of the half-shade field) it was found that not only were color effects absent but the match point of the field was very sharp. Measurements were therefore carried out in this way. Because of the excellent agreement shown in Table I between the author's and Cotton and Mouton's very reliable values for  $C_m$ , and the small dispersion of the substances investigated (Table II), it is considered appropriate to associate the various constants listed in Table II with  $\lambda = 578 \text{ m}\mu$ .

Psychological errors in the measurements were avoided as far as possible by the employment of two observers; one matched the optical field while the other recorded the corresponding deflection of the spring regulating the tension on the compensating strip. It was not until after a complete set of readings for a given specimen was made that the calibration curve was plotted and the value of  $\Delta T_2$  calculated. (Because of the presence of small residual double refraction, slight variations were found in the calibration curves for different specimens, and hence calibration readings were taken in every case before measurements were made with the magnetic field applied.)

An idea of the purity of the liquids examined, can be obtained from column (9) of Table II which indicates their source, the range in which the manufacturer specified their boiling point to lie, and whether or not they were distilled immediately before use. The three liquids which are noted as having received special treatment were prepared as follows. Sample (3) of methyl alcohol was treated with  $\text{AgNO}_3$  to change the aldehydes present to acids and with  $\text{KOH}$  to neutralize the acids thus formed; a fractional distillation was then made. Sample (1) of "absolute" ethyl alcohol was refluxed over solid calcium oxide for five hours to remove traces of moisture and then distilled in the presence of dry air. Ethyl ether, supplied by the Merck Chemical Company, and specified

TABLE I. *Results.*

Liquid	Values	$\Delta T_2$	Mean	$C_m$	
				Boorse	Cotton-Mouton
Acetone	25.0	25.0	25.0	+1.60	+1.6
Ethylene dichloride	31.5	33.5	32.5	-2.08	-2.1
Chloroform	43.5	43.5	43.5	-2.78	-2.8
Nitromethane	56.0	56.0	56.0	+3.58	+3.6

TABLE II. Cotton-Mouton constant for various liquids.  
Scale: Acetone = 1.60;  $t = 22^\circ\text{C}$ .

Liquid	Formula	$\Delta T_2$	$C_m$			$C_m/d$	$C_m(\text{abs.}) \times 10^{14}$	Chemical information
			Boorse	Chin- chalkar	C.S.			
Water	H·OH	6.6±0.8	-.15	-.15	-.14 <sup>1</sup>	-.14	-.37	Distilled
Methyl alcohol (1)	CH <sub>3</sub> ·OH	15.0±0.5	-.33	-.57		-.42		Mallinckrodt's "absolute"
Methyl alcohol (2)		14.1±0.6	-.31			-.39		Baker's "absolute" (dis- tilled)
Methyl alcohol (3)		5.6±0.4	-.12			-.16	-.30	Chem. Dept. C.U.—99.5% special treatment
Ethyl alcohol (1)	C <sub>2</sub> H <sub>5</sub> ·OH	9.5±0.8	-.21	-.38	-.39 <sup>1</sup>	-.26	-.52	U. S. Industrial Chem. Co. special treatment
Ethyl alcohol (2)		9.4±0.6	-.21			-.26		Chem. Dept. C.U. "abso- lute"
<i>n</i> -Propyl alcohol	C <sub>3</sub> H <sub>7</sub> ·OH	13.3±0.5	-.29	-.58		-.37	-.71	Chem. Dept. C.U. distilled over sodium hydroxide
<i>n</i> -Butyl alcohol	C <sub>4</sub> H <sub>9</sub> ·OH	16.0±0.8	-.35	-.67		-.43	-.86	E.K.C. b.p. 116–118°C— distilled
<i>n</i> -Heptane	C <sub>7</sub> H <sub>16</sub>	21.4±0.8	-.47	-.77	-.50 <sup>2</sup>	-.69	-1.16	E.K.C. b.p. 98–98.5°C distilled
Ethyl formate	H·COO·C <sub>2</sub> H <sub>5</sub>	41.9±0.4	+ .92	+ .95		+1.00	+2.26	E.K.C. b.p. 54–55.5°C
Methyl acetate	CH <sub>3</sub> ·COO·CH <sub>3</sub>	37.4±1.1	+ .82	+ .81		+ .88	+2.02	E.K.C. b.p. 56.5–57°C "anhydrous"—distilled
Ethyl acetate (1)	CH <sub>3</sub> ·COO·C <sub>2</sub> H <sub>5</sub>	30.9±0.9	+ .68	+ .72		+ .75	+1.66	E.K.C. b.p. 76–77°C "an- hydrous"
Ethyl acetate (2)		30.7±0.9	+ .67					Merck's "Reagent"
<i>n</i> -Propyl acetate	CH <sub>3</sub> ·COO·C <sub>3</sub> H <sub>7</sub>	22.4±0.6	+ .49	+ .49		+ .56	+1.21	E.K.C. b.p. 99–102°C
<i>n</i> -Butyl acetate	CH <sub>3</sub> ·COO·C <sub>4</sub> H <sub>9</sub>	15.1±0.7	+ .33			+ .38	+ .81	E.K.C. b.p. 124–126°C
<i>n</i> -Amyl acetate	CH <sub>3</sub> ·COO·C <sub>5</sub> H <sub>11</sub>	10.4±0.7	+ .23			+ .26	+ .57	E.K.C. b.p. 145–147°C, distilled
Ethyl ether	C <sub>2</sub> H <sub>5</sub> ·O·C <sub>2</sub> H <sub>5</sub>	17.9±0.4	-.39	-.70		-.55	-.96	Merck's "anhydrous" spe- cial treatment
<i>n</i> -Butyl ether	C <sub>4</sub> H <sub>9</sub> ·O·C <sub>4</sub> H <sub>9</sub>	19.4±0.4	-.43			-.56	-1.06	E.K.C. b.p. 142–144°C

<sup>1</sup> Haque, C.R. **190**, 789 (1930).

<sup>2</sup> Extrapolated from Scherer, C.R. **192**, 1223 (1931).  
b.p. = boiling point.

as "anhydrous-distilled over sodium" was further treated with metallic sodium to dry it and then distilled under the same conditions as ethyl alcohol above.

### III. RESULTS

The Cotton-Mouton constants for the liquids investigated are listed in Table II. Column (4) of this table gives the values of the constants found by the author, column (5) the corresponding values found by Chinchalkar and column (6) values found by several of Cotton's students, reference to the original papers in the latter case being given in footnotes. Column (7) gives the specific birefringence (values in column 4 divided by the density of the liquid), and column (8) the absolute Cotton-Mouton constants calculated from the values given in

column (4) and the absolute constant of nitrobenzene,<sup>13</sup> *viz.*,  $2.46 \times 10^{-12}$  at  $20^\circ\text{C}$ ,  $\lambda = 578 \text{ m}\mu$ .

The values of  $\Delta T_2$  listed in column (3) represent the average of from four to nine separate determinations. The maximum difference between *single* determinations in any set was 3.0 grams, and the minimum, 1.0 gram. Methyl alcohol sample (3) showed the smallest path difference of all the liquids examined; from the known values of  $L$ ,  $H^2$  and its absolute Cotton-Mouton constant, we may write in virtue of Eq. (2):

$$\Delta \equiv d/\lambda = 0.30 \times 10^{-14} \times 20 \times 5.1 \times 10^8,$$

where  $d$  represents path difference in cm. From the precision of the measurements of  $L$ ,  $H^2$ ,  $C_m$  for methyl alcohol (obtained from the precision

<sup>13</sup> Salceanu, C.R. **190**, 737 (1930); **191**, 486 (1930).



of  $\Delta T_2$  for this liquid and acetone) and  $C_m(\text{abs.})$  for nitrobenzene, estimated at less than 1 percent from Salceanu's paper:

$$\begin{aligned}d &= 3.06 \times 10^{-5} \lambda \pm 12 \text{ percent} \\ &= 1.8 \pm 0.2 \times 10^{-9} \text{ cm.}\end{aligned}$$

From the standpoint of the precision of the *optical measurements alone*, it would appear that since  $\Delta T_2$  for this methyl alcohol sample was determined to within about 7 percent (see Table II),

$$d = \lambda/32,000 \pm \lambda/450,000,$$

provided no systematic errors were present.

Inspection of Table II shows that there is good agreement between Chinchalkar's and the author's values of  $C_m$  in the case of substances having positive constants; the negative constants, however, show a systematic difference of about 0.3 in all liquids except water and ethyl alcohol. All measurements on the former of these two substances show excellent agreement, especially in view of the fact that the precision of the determinations is uniformly low. From the papers of Chinchalkar and Haque their precision appears to be about 20 percent, hence the fact that Haque's measurements were made at 16.6°C with the green line of mercury need not be taken into consideration in the comparison, since temperature and dispersion effects are not comparable with this experimental error.

As regards the case of ethyl alcohol Chinchalkar and Haque are also in agreement, while the value reported here is roughly 50 percent different. Neither of these investigators reports the estimated purity of his alcohol nor lists any special precaution taken in its purification. (Haque's measurements were made under the same conditions as his water determination.) As both methyl and ethyl alcohol are difficult to secure in a highly-purified anhydrous state, it seems desirable that further measurements be made on samples of known purity.

Further evidence of systematic variation between the negative constants obtained by Chinchalkar and the author appears in the case of methyl alcohol. His reported value for this liquid is  $-0.57$ ; he secures the same value within the experimental error for the constant of  $n$ -

propyl alcohol given as  $-0.58$ . The same kind of agreement can be noted in column (4) Table II if comparison is made between the constant found for a commercial sample of absolute methyl alcohol (distilled before use) with that of  $n$ -propyl alcohol. General evidence<sup>7, 8</sup> shows that a lengthening of the aliphatic carbon-hydrogen chain, provided unsaturated valence bonds are not thereby introduced, acts to increase negative or to decrease positive birefringence. By examining the values of the specific birefringence, it is evident that the acetates are in accord with this generalization; the alcohols will also be if the value of  $C_m$  for methyl alcohol is chosen as  $-0.12$ . This choice would also have been made from two other considerations: first, it places methyl alcohol between water and ethyl alcohol as regards specific birefringence, second, it is the most probable value on the grounds of the chemical purity of the three methyl alcohol specimens.

The value of the Cotton-Mouton constant for  $n$ -heptane can be extrapolated from Scherer's measurements on five members of the saturated hydrocarbon series  $C_nH_{2n+2}$  between  $C_8H_{18}$  and  $C_{14}H_{30}$ . The average difference between values of  $C_m$  for successive members of this series is 0.10 and  $C_m$  for  $C_8H_{18}$  is given as  $-0.6$ , so that on this basis  $C_7H_{16}$  should have a constant of  $-0.5$  for  $\lambda = 578 \text{ m}\mu$ . This is in good agreement with the value for  $n$ -heptane reported here.

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