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Magnetic Birefringence in Liquid Mixtures

By

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ABSTRACT.

The magnetic birefringence in liquid mixtures is known to show large deviations from theoretically expected values, and no explanation of these variations has so far been given. In order to investigate into this problem, magnetic birefringence in twenty-one binary liquid mixtures has been studied. The double refraction was estimated by measuring the shift of the dark band in Rayleigh's bent glass plate compensator. The results (Tables and curves 1 to 21) which are consistent with those of the previous workers, have the following chief features:—Curves for aniline, benzene, and toluene are concave towards the axis of concentration (in partial volumes), those for ethyl benzene, bromo-benzene and chloro-benzene are nearly straight, while those for CS_2 and nitrobenzene are convex, the gradual variation in the curvatures following the above order of the liquids; the different liquids mixed with the above ones change the curvatures slightly, keeping the essential features the same; there is an asymmetry in the curves for aniline. The curves to be expected on Langevin's theory are also drawn.

The experimental curves are correlated with the existing data on (1) temperature variation of magnetic birefringence. (2) temperature variation of molecular optical anisotropy and (3) optical anisotropy in the vapour and liquid states. From the striking correspondence between these different data, it is suggested that the variation in the effective optical anisotropy of the molecules with dilution is at least one, and probably the main, cause of the deviations observed in the birefringence in mixtures. The physical interpretation of the variations is discussed.

1. *Introduction.*

Magnetic birefringence in mixtures of organic liquids has been studied by Cotton and Mouton[1] and by Szivessy and Richartz.[2] The substances used by them were two nitro-compounds (nitro-benzene and nitro-toluene) and two halogen compounds (α-chloro-naphthalene and α-bromo-naphthalene), these being mixed with different organic liquids, both aliphatic and aromatic. These authors found that in almost all the cases the experimental values differed much from those to be expected on theoretical grounds, and no explanation or correlation of these departures has so far been put forward. The present investigation was undertaken as an attempt to try to understand the cause of these variations and to see if any light could be thrown on them by extending the available information with further experiments and by trying to correlate the observed variations with other existing data about these substances.

2. *The Law of Mixtures on Langevin's Theory.*

The Cotton-Mouton constant C of magnetic birefringence is defined by

$$C=\frac{n_p-n_s}{\lambda H^2} \qquad \dots \qquad \dots \qquad \dots \quad \text{(i)}$$

where n_p and n_s are the refractive indices of the liquid for light vibrations parallel and perpendicular to the applied magnetic field, λ the wave length of light used and H the strength of the magnetic field. Langevin's theory of magnetic birefringence assumes a magnetic as well as an optical anisotropy for the molecules of the liquid exhibiting the birefringence.

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[1] Cotton and Mouton, C.R., *156*, 1456 (1913); Ann. Chim. Phys., *30*, 321 (1913).

[2] Szivessy and Richartz, Ann. der Phys., *86*, 393 (1928).

Due to the magnetic anisotropy, the molecules tend to orientate themselves when placed in an external magnetic field, thermal agitations opposing, and this tendency to orientate makes the liquid doubly refracting to a small extent due to the optical anisotropy of the molecules. In calculating[3] an expression for C on this theory, the number of molecules per unit volume which will orientate with their axes having a definite inclination to the external magnetic field is calculated according to the Maxwell-Boltzmann expression, and thence the double refraction in the medium due to this orientation. The effect is then averaged over all the molecules. In the case of mixtures of liquids[4] the same treatment is given to the molecules of each kind separately, and the average optical moments contributed by a molecule of each kind per unit field of the incident light wave when the light vibrations are parallel and perpendicular to the magnetic field applied, are calculated. Let these be M'_p and M'_s for the molecules of kind 1, M''_p, M''_s, for kind 2 and so on. If $\nu_1, \nu_2, \ldots\ldots$ are the numbers of molecules of 1st, 2nd...kind per unit volume of the mixture, the moments P_p and P_s per unit volume of the mixture are

$$P_p = \nu_1 M'_p + \nu_2 M''_p + + \ldots = \frac{\nu_1}{N_1} . N_1 M'_p + \frac{\nu_2}{N_2} . N_2 M''_p + + \qquad \text{(ii)}$$

$$P_s = \nu_1 M'_s + \nu_2 M''_s + + \ldots = \frac{\nu_2}{N_2} N_1 M'_s + \frac{\nu_2}{N_2} N_2 M''_s + + . \qquad \text{(iii)}$$

where N_1, N_2,... are the number of molecules per unit volume in pure liquids. According to the Lorentz formula

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[3] Debye, Handbuch der Radiologie, Bd. VI, p. 769.

[4] Bergholm—Archiv. f. Mat. Astr. and Fys., Bd. 12, No. 3 (1917).
Szivessy—Zeit. f. Phys., 7, 285 (1921).
Bergholm has calculated the relation for the electrical double refraction. The effect of permanent electric moments was not taken note of when he gave the formula and the results are valid for the magnetic case also.

we have the relations

$$\left.\begin{array}{l} \dfrac{n_p^2-1}{n_p^2+2}=\tfrac{4}{3}\pi P_p \ ; \quad \dfrac{n'^2_p-1}{n'^2_p+2}=\tfrac{4}{3}\pi N_1 M'_p \ ; \ \text{etc.} \\[2ex] \dfrac{n_s^2-1}{n_s^2+2}=\tfrac{4}{3}\pi P_s \ ; \quad \dfrac{n'^2_s-1}{n'^2_s+2}=\tfrac{4}{3}\pi N_1 M'_s \ ; \ \text{etc.} \end{array}\right\} \qquad \text{(iv)}$$

where n's represent the refractive indices. Subtracting (iii) from (ii) and using eqns. (iv), and remembering that n_p's and the corresponding n_s's are nearly equal, we get

$$\frac{(n_p-n_s)n}{(n^2+2)^2}=\frac{\nu_1}{N_1}\ \frac{(n'_p-n'_s)n_1}{(n_1{}^2+2)^2}+\frac{\nu_2}{N_2}\ \frac{(n''_p-n''_s)n_2}{(n_2{}^2+2)^2}++ \qquad \text{(v)}$$

where n, n_1,...represent the mean refractive indices. If m_1, m_2, etc., are the number of grams of liquids 1, 2,...per c.c. of the mixture, and if d_1, d_2...are their densities, the partial volumes v_1 $\left(=\dfrac{m_1}{d_1}\right)$, v_2 $\left(=\dfrac{m_2}{d_2}\right)$......of the liquids in the mixture are equal to ν_1/N_1, ν_2/N_2 ...occurring in (v). From this and using (i), (v) reduces to

$$C\frac{n}{(n^2+2)^2}=C_1v_1\frac{n_1}{(n_1^2+2)^2}+C_2v_2\frac{n_2}{(n_2{}^2+2)^2}+\ldots \qquad \text{(vi)}$$

where C is the Cotton-Mouton constant of the mixture, and C_1 C_2......are those of the liquids 1, 2,......For binary mixtures, with one component of the mixture having a negligible magnetic birefringence ($C_2=0$), the above reduces to

$$C=C_1v_1\frac{n_1}{(n_1{}^2+2)^2}\cdot\frac{(n^2+2)^2}{n} \qquad \text{(vii)}$$

3. *The Compensator.*

In his previous investigations[5] on magnetic birefringence, the author had used the stained glass half-shade compensator

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[5] Ind. Jour. Phys., Vol. VI, pp. 165 and 581; Vol. VII, p. 317.

for the measurement of the double refraction. Since in the present case, the birefringence to be measured was not so small as in the previous cases, a more quick and handy method was resorted to. The bent glass plate described by Lord Rayleigh[6] was here used to measure the double refraction. Ordinary glass under pressure (or tension) is known to behave like a negetive (positive) uniaxial crystal with the axis along the direction of pressure (tension) and the birefringence can be taken to be proportional to the pressure (or tension). In a long thin glass plate bent in its own plane, the different layers above and below the neutral axis will behave like a series of uniaxial positive and negative crystals respectively, with their axes parallel to the neutral axis. Also since the strain in the different layers is proportional to their distances from the neutral axis, the birefringence produced by the layers will also be proportional to their distances from it. If a beam of plane polarised light with its direction of vibration inclined at 45° to the neutral axis is allowed to pass through the plate and then examined with a crossed analysing nicol and a telescope focussed on the plate, there will be seen in the field of view a dark band corresponding to the light passing through the neutral axis which passes unmodified through the plate and is quenched by the analyser. On either side of this dark band the light will not be quenched as it is elliptically polarised due to the double refraction produced by those parts of the bent plate, the sense of the ellipticity on the two sides of the band being opposite. If now the incident light is elliptically polarised, having a phase retardation δ_1 between light vibrations parallel and perpendicular to the neutral axis, the light will be made plane polarised by that layer of the plate which produces a retardation equal and opposite to δ_1, the dark band shifting to that place. From what has been said above, it can be seen that the sign and

[6] Rayleigh, Phil. Mag., 4, 680 (1902).
Szivessy, Handbuch der Physik., Bd. 19, p. 949.

magnitude of the shift will thus determine the sign and magnitude of the phase difference between the incident light vibrations parallel and perpendicular to the dark band, so long as the bending moment applied to the ends of the plate is unchanged. Thus all that is necessary to measure the relative birefringence in the case of mixtures with different concentrations for a given pair of liquids is to measure the shifts produced by these mixtures, keeping the bending moment of the plate constant.

For a given bending moment a strong source of light will be preferable in order that the parts of the plate very near to the neutral axis should restore an appreciable amount of light, making the dark band narrow. The range of the instrument as also the sharpness of the dark band can be increased by increasing the bending moment, when, however, the shift for a given birefringence, *i. e.*, the sensitivity, will become smaller. On the other hand, the use of too low a bending moment for increasing the sensitivity makes the band broad and diffuse, introducing an uncertainty in its location. Hence the proper amount of bending for a series of mixtures of a given pair of liquids can be chosen by considering all these factors, *viz.*, the strength of the course of light available, the breadth of the beam, the shift for a given birefringence and the range of the values required to be measured.

The actual strip of glass used was about 10·5 cms × 1 cm. bent in its own plane by the pressure applied at its ends. The thickness of the plate was about 1·5 mm. Suitable thin rubber pads were given below to ensure an even distribution of pressure at the points of application.

4. *Experimental.*

The other experimental arrangement was the same as in the author's earlier work.[7] The strong source of light was a

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[7] S. W. Chinchalkar, Ind. Jour. Phys., 6, 165 (1931).

1000 c. p. pointolite lamp, the light from which was condensed and collimated before passing through the polariser of which the principal direction of vibration was inclined at 45° to the horizontal. The direction of the magnetic field as well as the neutral axis was horizontal. The liquid mixtures were kept in stoppered glass tubes 33 cms. long with thin plane windows sealed to the ends. The tubes were kept in an equally long gap of the special electromagnet.[8] In all cases, a current of 11 amps. was used in the electromagnet giving a field of about 24000 gauss, except in the case of nitrobenzene where a lower current of about 4 amps. was found quite sufficient to give a large shift, of the same order as in the other liquids. The shift of the dark band was measured by means of an Adam Hilger micrometer eye-piece with which the observing telescope was fitted. The position of the centre of the band could be located to within one division of the micrometer scale. The mean of six or more readings was taken as the shift in each case. Considering the order of the shifts of the dark band in the various mixtures as given later (Tables 1 to 21) under results, one can get an idea of the sensitivity of the method. The deviations of the experimental values from the theoretical ones are far too large to be masked by, or even appreciably affected by, the errors in measurement, as can easily be seen from the curves. Test values were consistent when taken with different pure liquids and a comparison of the curves for nitrobenzene-CCl_4 mixtures with the same mixture investigated by Cotton and Mouton, shows that the two values agree very well (see Fig. 13).

The liquids used were of Kahlbaum's or Merck's manufacture. In most cases, one liquid was chosen to possess a high value of magnetic birefringence and the other almost negligible, so that from the birefringence point of view the one may

[8] M. Ramanadham, Ind. Jour. Phys., 4, 15 (1929).

be said to have been diluted by the other. The "diluents" were mostly carbon tetrachloride (Merck's extra pure or "Kahlbaum's") and cyclohexane, and in a few cases acetone. The cyclohexane used was tested with a sensitive half shade compensator and found to exhibit a feeble positive birefringence of the value of +0·03 as compared with +100 for nitrobenzene. Comparing this with the portion of the benzene-cyclohexane curve (Fig. 2) at infinite dilution and taking −0·5 as the value of magnetic birefringence for pure cyclohexane,[9] it is found that the sample of cyclohexane used contained about 1% of benzene as impurity.

According to equation (vii) the concentrations of the mixtures should be expressed in terms of the partial volumes of one component. If V_1 and V_2 c.cs. of two liquids on mixing give V as the volume of the mixture, the partial volume v_1 ($=V_1/V$) of liquid 1 is equal to $\frac{v_1}{v_1+v_2}$ provided the volume change produced on mixing is negligible. The diluents in most of our cases being non-polar, the volume changes were expected to be small. The volume changes in the mixtures proposed to be investigated were found out from available data (*e.g.*, International Critical Tables, Vol. III). It was seen that in most of the mixtures the maximum changes were of the order of 0·2 to 0·3 per cent. or even less, which were well within the accuracy of the measurement of the shift. It would have been indeed superfluous to take account of the changes in these cases. Where the changes were larger than these, due corrections were made, the mixtures being in all cases made by weights.

5. *Results.*

The results for the twenty-one mixtures studied are given in the tables (1 to 21) at the end of the paper. The

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[9] Scherer, C. R., *192*, 1223 (1931).

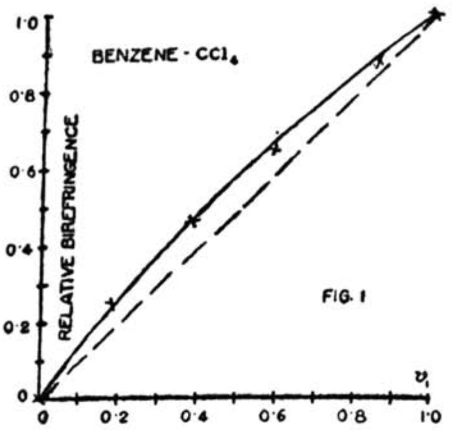


FIG. 1

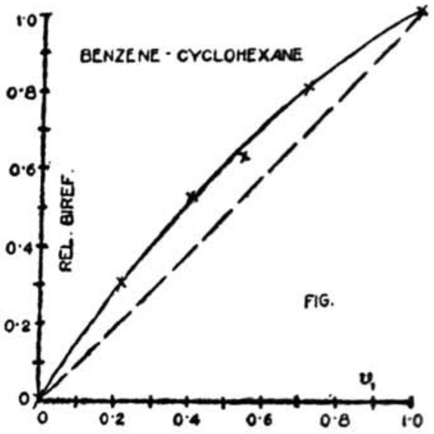


FIG.

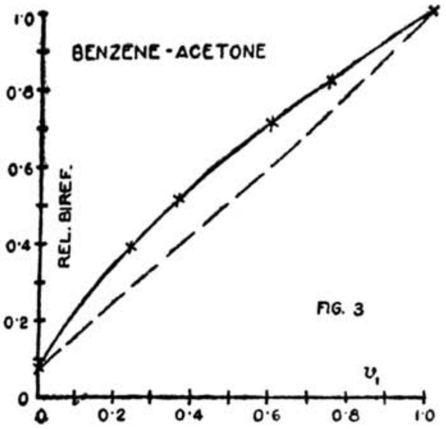
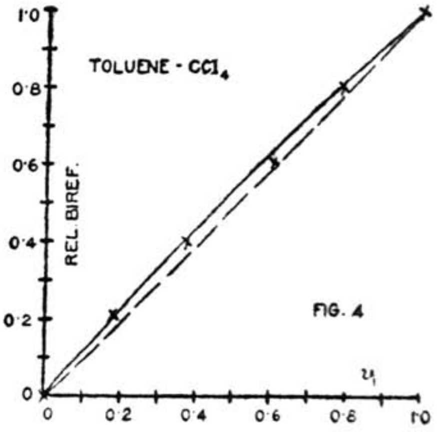


FIG. 3



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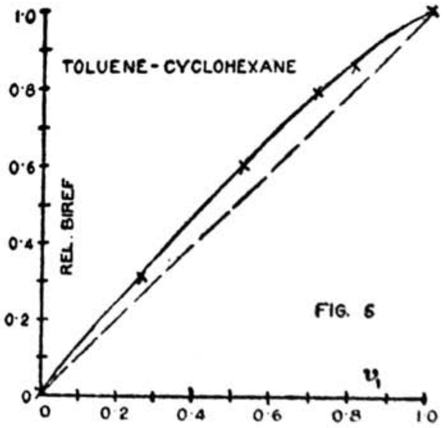


FIG. 5

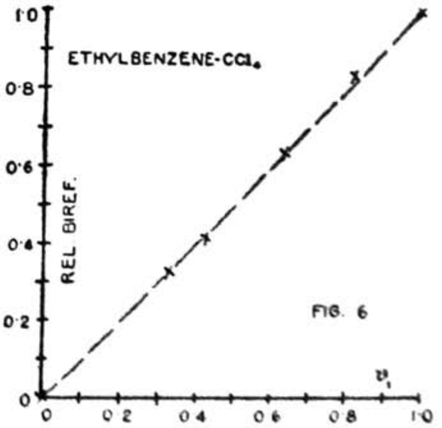


FIG. 6

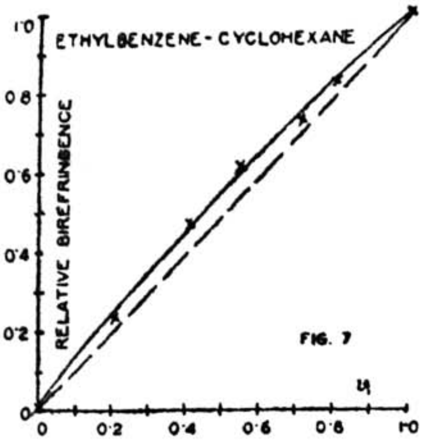


FIG. 7

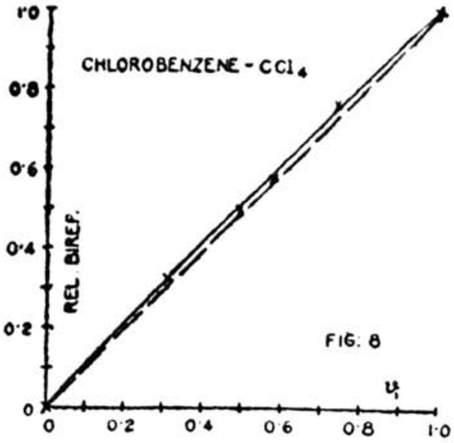


FIG. 8

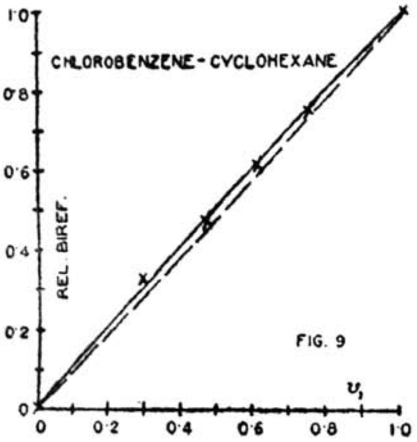


FIG. 9

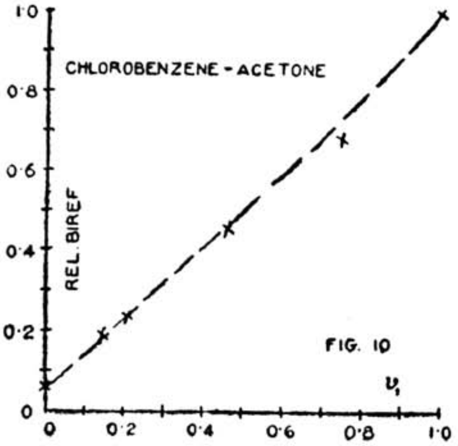


FIG. 10

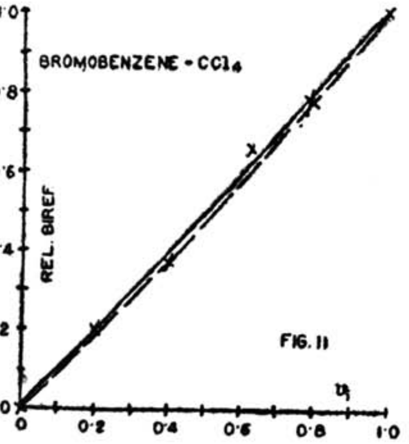


FIG. 11

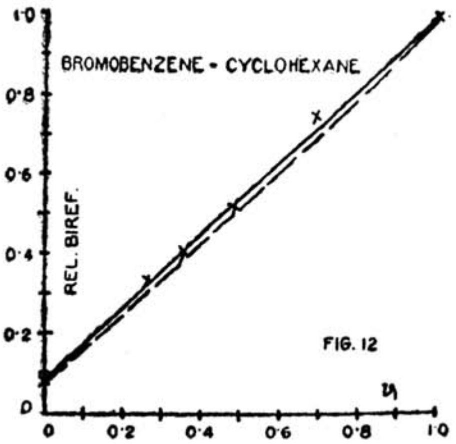


FIG. 12

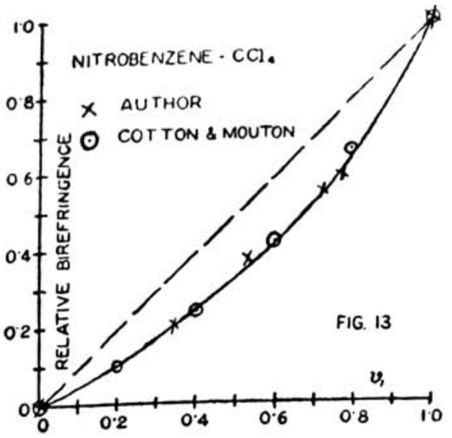


FIG. 13

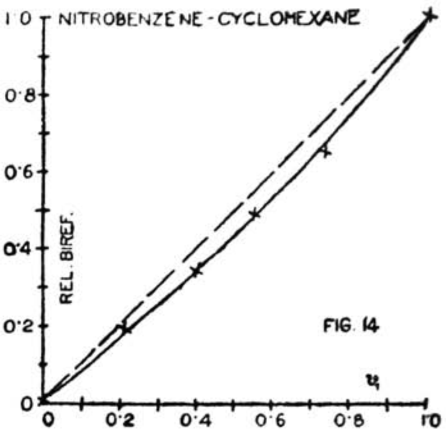


FIG. 14

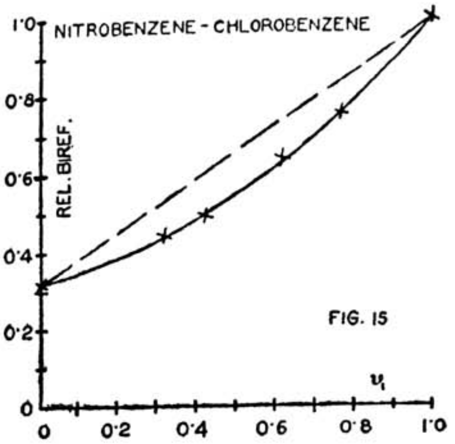


FIG. 15

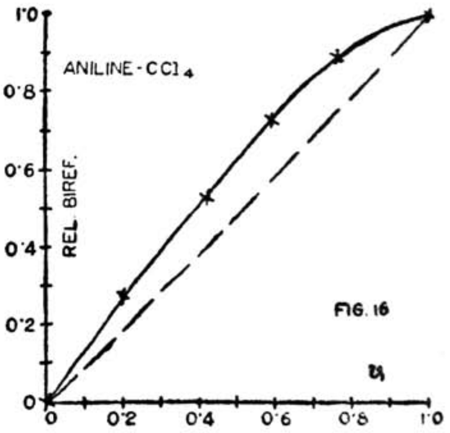


FIG. 16

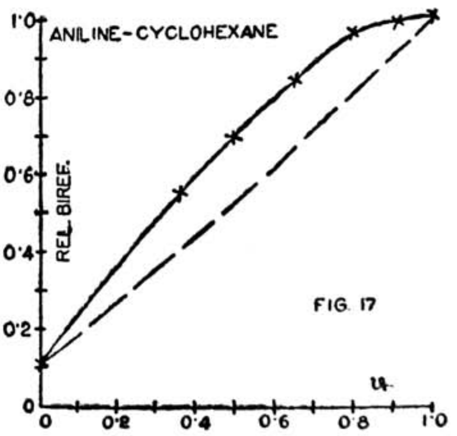
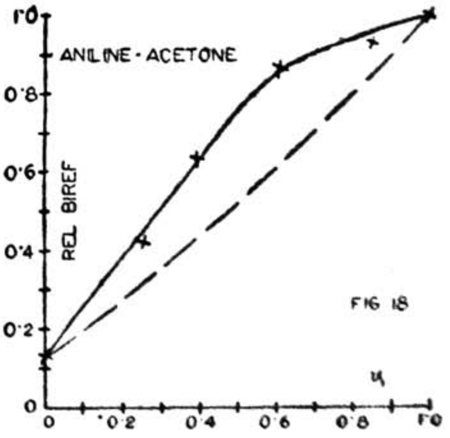


FIG. 17



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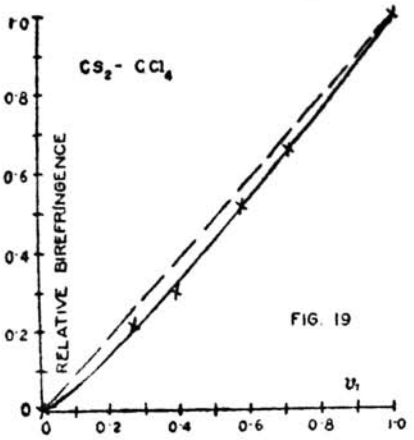

FIG. 19

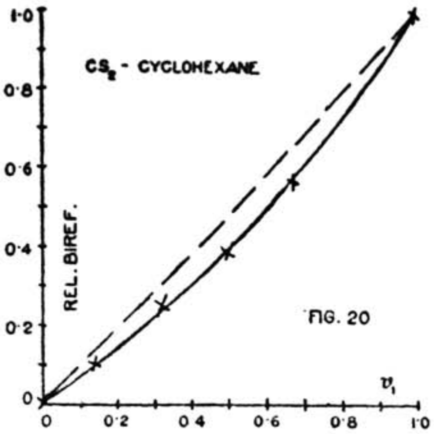

FIG. 20

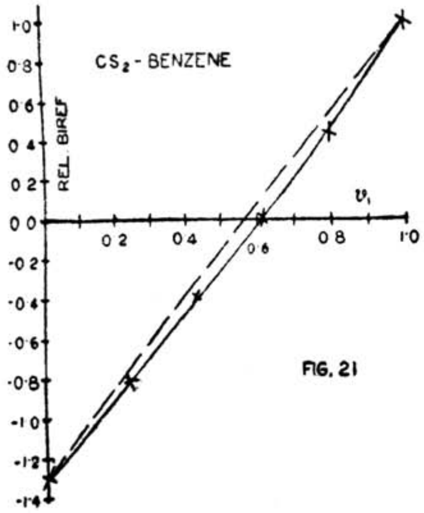

FIG. 21

first column of the tables gives the partial volumes of the first-named liquid in the pair constituting the mixtures; the second column gives the shift of the dark band in micrometer screw divisions, it being proportional to the birefringence; the third column gives the relative birefringence assuming the value unity for the mixture with partial volume 1. In the curves this relative birefringence is plotted against the partial volumes. This secures the same relative value of maximum birefringence for all the mixtures; and a glance at the curves gives an idea of the relative deviations for the different cases. The curves theoretically expected (eq. vii) are drawn by broken lines. The refractive index n of the mixture used to calculate the theoretical values was calculated from the concentrations of the mixtures by Lorentz formula. It was verified from available data of refractive indices of mixtures that the use of the actual experimental value of n for a given mixture instead of that calculated from the Lorentz formula does not alter the factor $\left\{\frac{(n^2+2)^2}{n}\cdot\frac{n_1}{(n_1^2+2)^2}\right\}$ occurring in equation (vii) to an appreciable extent. The theoretical curves vary only slightly from a linear relation ; hence the theoretial values have not been given in the tables.

6. *Discussion.*

On examining the different curves, it is seen that (*a*) mixtures of benzene, toluene and aniline exhibit curves concave towards the axis of concentration, those of nitrobenzene and carbon disulphide are convex, while those of chloro- and bromo-benzene and ethyl-benzene more or less agree with the theoretical curves and are almost straight ; (*b*) any of the "diluents" used keeps the essential nature of the curve of a given liquid the same, though in several cases it is found that when cyclohexane is used as a diluent, the curves are a little less convex (or more concave) towards the concentration axis than when carbon tetrachloride was used ; (*c*) a gradual diminution is found in the concavity of the curves towards the concentration axis in the benzene derivatives in the following order :—benzene, toluene, ethylbenzene, bromobenzene, chlorobenzene and nitrobenzene, the change being rather sudden in the case of nitrobenzene ; (*d*) there is a pronounced asymmetry in the curves of aniline (Figs. 16-18), the rate of diminution of magnetic birefringence with dilution being very small up to about 75% volume concentration, and thereafter increasing markedly. On examining the results of earlier workers, one finds that many of these essential features are to be seen in their work also. Thus, Cotton and Mouton[1] found the nitrobenzene curves convex when ethyl school, acetone and dibromoethane were used as diluents, agreeing with (*b*) above. Results of Szivessy and Richartz[2] show that curves for nitrobenzene and nitrotoluene were fairly convex, but those with chloronaphthalene (analogous to our chlorobenzene) have very little curvature, being almost straight and close to the theoretical curves ; this agrees with our (*c*).

According to Langevin's theory of magnetic birefringence the molecules of the liquid are optically as well as magnetically anisotropic. Apart from their anisotropies, in a dense fluid like a liquid, the behaviour of the molecules would be modified by the influence of the neighbouring molecules also. Thus, if the molecules are electrically polar, the phenomena of molecular association would be a prominent feature of the intermolecular influences. Even in non-polar substances, Raman and Krishnan[10] have shown that the effect of the non-symmetrical shape of the molecules results in the polarisation field at a molecule due to the surrounding ones becoming anisotropic. Without going for the present into the cause and nature of the influence of the neighbouring molecules, we can take it that these do modify the observed properties of a given molecule. As a result of mixing some foreign liquid, the given liquid is rarefied, and the influence of molecules of its

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[10] *e. g.*, Raman and Krishnan, Phil. Mag., *6*, 498 (1928); Proc. Roy, Soc., A., *117*, 1 (1927).

own kind on a given molecule becomes smaller. Thus, for example, it is known that polar association tends to break up by dilution. A change in the physical conditions of a liquid which produces effects similar to " dilution " is the heating of a liquid and the ultimate case of vaporisation. The intermolecular influences are modified by heating, on the one hand, by a change of volume so that each molecule gets more space for itself, and on the other, if there is any sort of a regular order in a liquid as due to polar association or due to other forces like the " van der Waal forces," this order tends to be destroyed by the increasing thermal agitation. It would therefore be instructive to compare the temperature variation of those properties of liquids which are related to magnetic birefringence, with the variations of magnetic birefringence in mixtures. In making these comparisons and in all the discussions to follow, the following remark about the curvatures will always be remembered. From the point of view of Langevin's theory, the interpretation of the different curvatures is that for those cases where the concentration-birefringence curve is more convex (or concave) towards the concentration axis than the theoretical curve, the effective anisotropy of the molecules of the liquid, either optical or magnetic or both, is decreased (or increased) when the liquid is " diluted."

7. *Relation with Temperature Variation of Magnetic Birefringence.*

Let us take first the variation of magnetic birefringence itself with temperature. According to Langevin's theory, the absolute temperature T, the refractive index n, the density d and the Cotton-Mouton constant C are connected by the relation

$$C = \frac{d(n^2+2)^2}{nT} k \tag{viii}$$

where k is a constant unaffected by temperature. The temperature variation of C for all the substances studied by the author for mixtures has not been investigated; but Szivessy[11] found that for nitrobenzene and chloro- and bromo-benzene the constant diminishes with increase of T, the rate of diminution being greatest for nitrobenzene. This shows that for nitrobenzene and others, the magnetic birefringence C diminishes much more rapidly with increase of temperature than is indicated by theory, *i.e.*, the effective molecular anisotropy diminishes with increase of temperature. We have not got data for temperature variation for benzene and toluene for which the birefringence-concentration curves have an opposite curvature to that for nitrobenzene. But recently, Salceanu[12] has studied the temperature variation of molten naphthalene which is two molecules of benzene joined together, and finds that for it the constant k does actually increase with temperature for temperatures not too near the melting point. He also finds that for β-methylnaphthalene, which stands in nearly the same relation to naphthalene as toluene to benzene, k does not change appreciably. Thus, the variation in k with temperature for the series naphthalene, β-methylnaphthalene, chlorobenzene and nitrobenzene can be seen to follow the same order as the variation in the curvatures of birefringence-concentration curves of the series benzene, toluene, chlorobenzene and nitrobenzene. With temperature variation or with dilution the magnetic birefringence does not diminish to the extent as indicated by theory in the cases of naphthalene and benzene; while it diminishes much more than is indicated by the theory, in the case of nitrobenzene. We cannot expect to get an exact quantitative agreement for each individual case unless we know how a change, for example, in dipolar association, effected by temperature variation is related to that made by dilution.

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[11] Szivessy, Ann. der. Phys., *68*, 127 (1922).

[12] Salceanu, C. R., *194*, 863 (1932).

8. *Relation with (a) Variation of Optical Anisotropy with Temperature and (b) Optical Anisotropy in Liquid and Vapour States.*

The magnetic birefringence is dependent on the optical anisotropy of the molecules and, according to Langevin's theory, is proportional to the differences in optical moments induced in a molecule in three mutually perpendicular directions, the constant k of equation (viii) being

$$k = \frac{\pi N}{135 \lambda \kappa M} \{(A-B)(A'-B') + (B-C)(B'-C') + (C-A)(C'-A')\} \quad \ldots \quad \text{(ix)}$$

where N is the Avogadro number, M the molecular weight of the liquid, κ the Boltzmann constant, A, B, C are the optical moments induced by a unit electrical field of the incident light wave acting respectively along the three mutually perpendicular directions of the optical ellipsoid of the molecule, and A′, B′, C′ are the magnetic moments induced by a unit magnetic field acting along the same three directions. The optical anisotropy of the molcules is defined by

$$\delta = \frac{(A-B)^2 + (B-C)^2 + (C-A)^2}{(A+B+C)^2} \quad \ldots \quad \text{(x)}$$

It would thus be instructive to compare the variation in the effective optical anisotropy of the molecules due to change in physical conditions, with our curves. δ is related to the depolarisation r of the transversely scattered light and the isothermal compressibility β of the liquid by the relation[13]

$$\delta_{\text{liq}} = \frac{RT\beta n}{N} \, \frac{10r}{6-7r} \quad \text{(xi)}$$

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[13] See Cabannes, La Diffusion Moleculaire de la lumiere, Paris, 1929, for discussion and fuller references.

where *n* is the number of molecules per c. c. For the case of a perfect gas (or vapour very approximately) this reduces to

$$\delta_{gas} = \frac{10r}{6-7r} \qquad \text{(xii)}$$

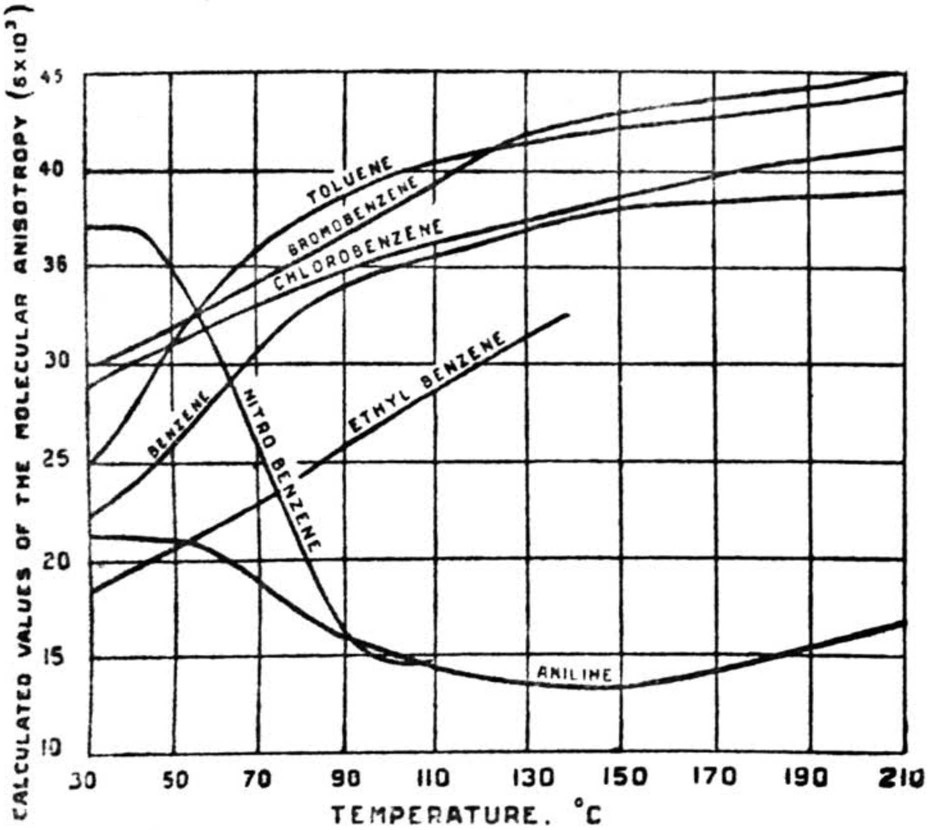

FIG. 22.

It is experimentally found that δ calculated for the molecules in the liquid state from eq. (xi) is usually different from δ for the same molecules in the vapour state calculated from (xii), the difference being due to the inter-molecular influences in the closely packed liquid state. When a liquid is heated $\delta_{liq.}$ would change and ultimately reach the δ_{gas} value when it is vapourised. Without again going just now in the cause of these variations, let us compare the temperature variations in $\delta_{liq.}$ for different liquids with our curves. The temperature variation of δ has been studied by Ramachandra Rao [14] for seven of the eight liquids used in the present investigation, *viz.*, benzene, toluene, ethylbenzene, chloro- and bromo-benzene, nitrobenzene and aniline. His curves are reproduced here (Fig. 22). While discussing the data about light scattering in fluids, Krishnan [15] has given values for δ_{liq} for carbon disulphide at different temperatures taken from unpublished results of Ramanathan. Of the two series of value given by him based on two different formulæ used in the calculations, the values from the one that has been accepted

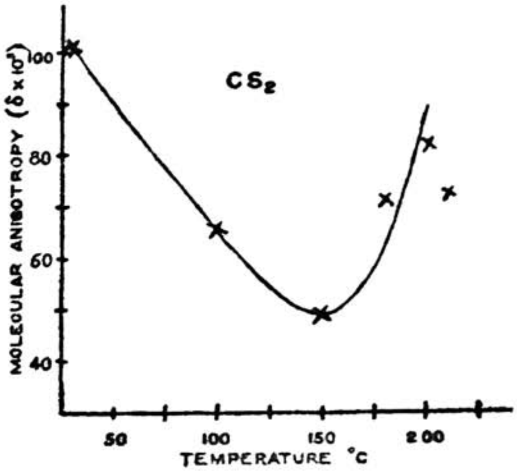

FIG. 23.

at present (eq. xi) are taken, and Fig. 23 represents the curve drawn from those values. The values of $\delta_{liq.}$ when the temperature is further increased will asymptotically tend to reach the value for $\delta_{vap.}$; and hence comparison of $\delta_{liq.}$ and $\delta_{vap.}$ for these substances should be taken note of in conjunction with the above curves. In Table 22 are given the values of $\delta_{liq.}$ and $\delta_{vap.}$ for the eight liquids used, after I. Ramakrishna Rao. [16]

[14] S. Ramachandra Rao, Ind. Jour. Phys., 3, 21 (1928).

[15] K. S. Krishnan, Proc. Ind. Assn. Cult. Sc., 9, 268 (1926).

I. Ramakrishna Rao, Ind. Jour. Phys., 2, 61 (1927).

TABLE 22.

Substance.	Benzene.	Toluene.	Ethyl benzene.	Chloro-benzene.	Bromo-benzene.	Aniline.	Nitro-benzene.	CS_2.
δ liq. × 10^3	22	22	21·9	27	31	21·7	53	106
δ vap. × 10^3	39·1	43·7	41·5	43·9	46·9	54·7	50	106

It is interesting to find that only in the two cases of nitrobenzene and carbon disulphide for which the birefringence concentration curves are convex towards the axis of concentration do we find the optical anisotropy of molecules in the liquid and vapour states to be practically the same. Again for these two liquids only is $\delta_{\text{lid.}}$ found at first to diminish to a great extent with the increase of temperature, and then to begin to increase. Even at temperatures much higher than those reached in Figs. 22 and 23, the value of $\delta_{\text{liq.}}$ would only tend to approach the $\delta_{\text{vap.}}$ value, being actually always less than it. Since $\delta_{\text{liq.}}$ is nearly the same as $\delta_{\text{vap.}}$ for these two, it is seen that with the increase of temperature, the optical anisotropy $\delta_{\text{liq.}}$ of the molecules will always be less than that at room temperature. A similar diminution of the effective optical anisotropy with dilution would give for nitrobenzene and carbon disulphide curves like the experimental ones.

For the other liquids for which the birefringence curves are concave towards the concentration axis or nearly straight, $\delta_{\text{liq.}}$ is found to increase with temperature. Apparently for the case of aniline, the temperature variation curve shows a slight and gradual diminution up to about 140° after which however $\delta_{\text{liq.}}$ has begun to increase, but on looking at its $\delta_{\text{vap.}}$ value which is much higher than $\delta_{\text{liq.}}$ one can see that for further increase of temperature, $\delta_{\text{liq.}}$ will increase rapidly and become more than that at room temperature.

The curve for aniline in Figure 22 is only an initial part and not fully representative. In fact, the difference between $\delta_{\mathrm{vap.}}$ and $\delta_{\mathrm{liq.}}$ for aniline is much greater than that for any of the other seven liquids, for many of which $\delta_{\mathrm{liq.}}$ increases rapidly with temperature. Thus, the temperature—$\delta_{\mathrm{liq.}}$ curve for aniline taken together with the difference in $\delta_{\mathrm{vap.}}$ and $\delta_{\mathrm{liq.}}$ values is fully consistent with the nature of its birefringence-concentration curve which is concave towards the concentration axis, according to the arguments developed above.

On comparing the $\delta_{\mathrm{liq.}}$-temperature and the birefringence-concentration curves a striking similarity is again found in the variations of the general slopes of the former curves and the variations in the curvatures of the latter curves as we pass from benzene, through toluene, ethyl benzene, bromo-benzene and chlorobenzene to nitrobenzene. The rate of increase of $\delta_{\mathrm{liq.}}$ with temperature decreases after benzene and toluene and ultimately becomes negative in nitrobenzene; this corresponds to the curvature of the birefringence curve of benzene which becomes less for toluene, ethyl benzene and bromo- and chloro-benzene and ultimately reverses for nitrobenzene. In benzene, the magnetic birefringence in a diluted state has a value higher than that indicated by theory and this corresponds to the higher values of $\delta_{\mathrm{liq.}}$ for benzene molecules with increase of temperature. For nitrobenzene, the opposite is the case both for $\delta_{\mathrm{liq.}}$ as well as for birefringence. In these comparisons again, as in the previous ones for temperature variation of birefringence, we do not expect a strict quantitative correspondence for each case.

9. *Conclusion from the Preceding Discussions.*

The different comparisons made so far are of experimental facts and do not rest on any particular theory about these variations. A more direct comparison, would be with change of optical anisotropy with dilution, but data about it are wanting at present. But the comparisons made and the striking similarities seen in the preceding paragraphs between birefringence in mixtures and data about three different phenomena, *viz.*, (1) temperature variation of magnetic birefringence, (2) temperature variation of the optical anisotropy of molecules and (3) the optical anisotropy of molecules in the liquid and gaseous states, seems definitely to indicate that the variation in the optical anisotropy is at least one, and probably the main, cause of the deviations of the values of magnetic birefringence of liquid mixtures from those to be expected theoretically.

10. *Remarks on the Physical Interpretation.*

When one tries to picture the mechanism of these variations, different factors have to be considered. In polar molecules, dipolar association plays an important part. It is well known that dilution breaks up the molecular association, and this breaking up of association will in general change the observed molecular anisotropy. Some peculiarities in his investigations have been attributed to molecular association by Ramachandra Rao. In our mixtures, the asymmetry of the aniline curves seems to be due to association, aniline being strongly polar. Probably the aniline molecules in the unassociated state have a higher effective magneto-optic anisotropy than in the associated state. When the liquid is diluted, in the initial stages the diminution of birefringence due to the diminution in the number of molecules is compensated for by the breaking up of association and the consequent increase in molecular anisotropy, and so in these stages, the rate of diminution of birefringence with dilution is small. Afterwards, when a large number of molecules have been broken up, the diminution due to dilution preponderates, and the rate of decrease of birefringence becomes large.

In non-polar substances also it is known that close packing as in liquids changes the molecular anisotropy, it being generally different from that in the vapour state. Raman and Krishnan[10] have shown that this can be explained as due to the non-symmetrical distribution of molecules round a given one, producing an anisotropy in the polarisation field at the given molecule due to the surrounding ones. This anisotropic polarisation field depends upon the non-symmetrical shape of the molecule and the closeness of approach of the surrounding molecules to it. In general, the effect is to diminish the molecular optical anisotropy. With increasing temperature, the molecules get more space for themselves and the distribution of molecules round a given one becomes more symmetrical, and the optical anisotropy increases. The temperature variation curves of the non-polar hydrocarbons have been shown to agree with those to be expected on the above ideas of the anisotropic polarisation field.[17] The temperature variation and dilution, however, stand on a different footing so far as the above theory of anisotropic polarisation field is concerned. When the temperature is increased, due to the greater free space available the region of approach of the surrounding molecules to a given one become more nearly symmetrical, and the anisotropy of the polarisation field diminishes. But the effect of dilution is simply to replace the molecules surrounding a given one from its own kind to that of the diluent; but the distribution of the molecules of the second liquid and the consequent polarisation field will still remain unsymmetrical, this being dependent only on the shape of the given molecule. If, however, we assume that the diminution in the optical anisotropy is due not merely to the unsymmetrical distribution round a given one, but also to some kind of temporary molecular grouping in the liquid state, then the breaking up of this temporary grouping both

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[17] Krishnan and Ramachandra Rao, Ind. Jour. Phys., 4, 39 (1929).

due to an increase of temperature and due to dilution would explain the general correspondence between the two phenomena observed above. Such temporary grouping has also been suggested from X-ray diffraction in liquids and other observations.[18] Experimental study of variation of optical anisotropy in mixtures would also throw light on the points raised here.

In conclusion, the author desires to express his heartfelt thanks to Professor Sir C. V. Raman, Kt., F.R.S., N.L., for his keen interest and kind encouragement. Thanks are also due to the King Edward Memorial Society, Nagpur, for having extended the term of the Research Scholarship.

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e.g., **Stewart**, Phys. Rev., 32, 558 (1928). K. Banerjee, Ind. Jour. Phys., **4**, 541 (1930).

TABLES.

v_1.	Shift.	Relative Birefringence.	v_1.	Shift.	Relative Birefringence.
1 Benzene-CCl_4			4 Toluene-CCl_4		
0	0	0	0	0	0
0·176	21·0	0·251	0·177	14·5	0·204
0·378	38·5	0·461	0·372	28·5	0·401
0·583	53·5	0·641	0·606	43·0	0·606
0·850	73·0	0·874	0·787	57·0	0·803
1	83·5	1	1	71·0	1
2 Benzene-Cyclohexane			5 Toluene-Cyclohexane		
0	insensible	...	0	insensible	...
0·215	19·0	0·306	0·265	21·5	0·307
0·395	32·5	0·529	0·523	42·0	0·600
0·541	39·0	0·634	0·708	55·5	0·793
0·712	50·0	0·813	0·805	60·0	0·857
1	61·5	1	1	70·0	1
3 Benzene-Acetone			6 Ethyl benzene-CCl_4		
0	6·0	0·080	0	0	0
0·237	29·0	0·387	0·332	27·0	0·329
0·357	38·0	0·507	0·427	34·0	0·415
0·588	53·0	0·707	0·639	52·0	0·634
0·737	61·5	0·820	0·819	68·0	0·829
1	75·0	1	1	82·0	1

TABLES (*contd.*).

c_1.	Shift.	Relative Birefringence.	c_1.	Shift.	Relative Birefringence.
7 Ethyl benzene-Cyclohexane			10 Chlorobenzene-Acetone		
0	insensible	...	0	6·5	0·063
0·205	18·0	0·234	0·145	19·5	0·187
0·410	36·0	0·468	0·210	24·5	0·234
0·543	47·5	0·617	0·462	46·0	0·448
0·712	56·0	0·727	0·750	69·5	0·678
0·800	63·5	0·825	1	97·5	1
1	77·0	1			
8 Chlorobenzene-CCl_4			11 Bromobenzene-CCl_4		
0	0	0	0	0	0
0·313	28·0	0·326	0·198	20·0	0·203
0·496	42·5	0·494	0·397	36·5	0·370
0·481	49·5	0·576	0·626	65·0	0·660
0·788	65·5	0·762	0·788	76·5	0·777
1	86·0	1	1	98·5	1
9 Chlorobenzene-Cyclohexane			12 Bromobenzene-Cyclohexane *		
0	insensible	...	0	8·0	0·080
0·287	28·0	0·331	0·260	33·5	0·337
0·466	40·0	0·473	0·356	40·5	0·407
0·606	52·0	0·615	0·485	51·5	0·518
0·747	63·5	0·752	0·690	74·5	0·749
1	84·5	1	1	99·5	1

* The sample of cyclohexane used for these two mixtures had an appreciable benzene impurity.

TABLES (*contd.*)

v_1.	Shift.	Relative Birefringence.	v_1.	Shift.	Relative Birefringence.
13 Nitrobenzene-CCl_4			16 Aniline-CCl_4		
0	0	0	0	0	0
0·342	14·0	0·207	0·197	20·0	0·274
0·526	25·5	0·378	0·418	38·5	0·528
0·717	37·0	0·548	0·592	53·0	0·726
0·778	40·0	0·593	0·761	65·0	0·890
1	67·5	1	1	73·0	1
14 Nitrobenzene-Cyclohexane			17 Aniline-Cyclohexane*		
0	insensible		0	8·0	0·112
0·211	12·0	0·189	0·358	39·0	0·549
0·400	21·5	0·339	0·490	49·0	0·690
0·554	31·0	0·488	0·652	59·5	0·838
0·736	41·0	0·646	0·793	68·0	0·957
1	63·5	1	0·912	69·5	0·979
			1	71·0	1
15 Nitrobenzene-Chlorobenzene			18 Aniline-Acetone		
0	28·5	0·305	0	9·0	0·126
0·318	41·0	0·439	0·251	30·0	0·420
0·422	45·5	0·487	0·390	45·5	0·636
0·615	59·5	0·637	0·615	62·0	0·867
0·768	70·0	0·749	0·851	66·5	0·930
1	93·5	1	1	71·5	1

TABLES (*contd.*)

v_1.	Shift.	Relative Birefringence.	v_1.	Shift.	Relative Birefringence.
	19 CS_2-CCl_4			20 CS_2-Cyclohexane	
0	0	0	0	insensible	
0·265	10·5	0·216	0·140	5·0	0·101
0·392	14·5	0·299	0·318	12·5	0·253
0·578	25·0	0·515	0·496	19·0	0·384
0·708	32·0	0·659	0·673	28·0	0·566
1	48·5	1	1	49·5	1

v_1.	Shift.	Relative Birefringence.
	21 CS_2 – Benzene	
0	−58·5	−1·31
0·239	−36·0	−0·81
0·428	−17·0	−0·38
0·615	4·0	0·09
0·795	19·5	0·44
1	44·5	1

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