

# DISPERSION OF DEPOLARISATION OF RAYLEIGH SCATTERING.

## Part I. Fatty Acids.

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### 1. Introduction.

ALTHOUGH the state of polarisation of the light scattered transversely by a variety of substances has been studied in detail by numerous investigators, comparatively little work has been done on the dispersion of depolarisation with wave-length. Some early investigations carried out by K. S. Krishnan<sup>1</sup> on a large number of liquids using sunlight filtered through suitable coloured glasses did not show any large dependence of depolarisation on wave-length. These measurements should be taken as only preliminary, since the incident light was not strictly monochromatic, filters used transmitting fairly wide regions of the spectrum. A few years later K. S. Krishnan and A. Sircar<sup>2</sup> have reported the results of the measurements on the dispersion of polarisation of the light scattered by benzene both in the liquid state and in the state of vapour. It is found that while the depolarisation factor for the liquid remains constant over a wide range of wave-length the value for the vapour increases appreciably as we proceed towards the ultraviolet.

A. F. Turner<sup>3</sup> has studied in detail the dependence on wave-length of the intensity and depolarisation of the light scattered transversely by liquid benzene. But no appreciable dispersion of depolarisation has been reported by him. Very recently the depolarisation of the unmodified scattered light has been investigated by S. M. Mitra<sup>4</sup> in carbon disulphide and benzene over a wide range of wave-length, and it is found that the depolarisation factor is independent of wave-length for these two liquids. The investigators mentioned above restricted themselves to observations with a non-associated

<sup>1</sup> K. S. Krishnan, *Phil. Mag.*, 1925, 50, 697.

<sup>2</sup> K. S. Krishnan and A. Sircar, *Ind. Jour. Phys.*, 1931, 6, 193.

<sup>3</sup> A. F. Turner, *Inaugural Dissertation, Berlin University*, 1935.

<sup>4</sup> S. M. Mitra, *Zeits. f. Phys.*, 1935, 96, 29.

liquid such as benzene. Consequently in the absence of adequate data it is not justifiable to say that the depolarisation of the transversely scattered light is independent of wave-length. It has been observed that highly associated liquids show certain anomalies in light scattering<sup>5</sup>. Therefore it is not unreasonable to expect an appreciable dispersion of depolarisation in these liquids. In view of these circumstances, it was thought desirable to study the dependence of depolarisation of the unmodified scattering on wave-length in a series of associated as well as non-associated liquids. In this paper the results obtained with the first five members of the fatty acids and benzene are given.

## 2. *Experimental Details.*

The principle of the method is essentially the same as in the well-known Cornu method of measuring partially polarised light which has been very frequently used in light scattering, with this difference, *viz.*, the scattered light after passing through the double-image prism and nicol is analysed spectroscopically. A fused silica cross was used as the container for the liquid to be examined. The arms of the cross were each 3 inches long and  $1\frac{1}{2}$  inches in diameter with fused transparent quartz windows fused on to their ends. The cross was connected on to a pyrex flask through a quartz pyrex seal. The liquid was distilled dust free into this cross by the usual method of Martin. Chemically pure liquids were taken for the experiment. The cross was blackened on the outside excepting for three end faces.

The light from a point-light quartz mercury arc lamp was focussed at the centre of the silica cross containing the dust-free liquid. A quartz double-image prism (optical contact) was placed in the path of the transversely scattered light and it was so orientated as to deviate the rays passing through it in a vertical plane. Immediately behind it was the nicol (transmitting the ultraviolet region also) and further behind another quartz lens which focussed the two images of the track formed by the passage through the double-image prism on the slit of the spectrograph. The slit of the spectrograph was kept rather broad. The two images were well separated, one above the other, crossing the slit and corresponded to vibrations in the scattered light which were initially vertical and horizontal respectively. The spectrograph made use of in the present experiment was a small Hilger quartz spectrograph. In this arrangement the errors arising from the polarisation effects of the spectrograph were automatically eliminated. The nicol in the path of the scattered light was so orientated that the two images

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<sup>5</sup> I. Ramakrishna Rao, *Ind. Jour. Phys.*, 1927, 2, 61; S. Ramachandra Rao, *Ind. Jour. Phys.*, 1928, 3, 1; R. S. Krishnan, *Proc. Ind. Acad. Sci.*, A, 1936, 3, 126.

of the scattered light for a particular wave-length were of equal intensity. A photograph was taken for this position of the nicol. The nicol was slowly rotated step by step through a degree on either side and a series of photographs was taken for the successive orientations of the nicol. The following six liquids have been investigated thus, *viz.*, benzene, formic acid, acetic acid, propionic acid, normal butyric acid, and isobutyric acid.

### 3. Results.

In the case of benzene it was found that for one particular orientation of the nicol the two components of the scattered light were of equal intensity for the whole recorded spectrum. With a slight rotation of the nicol either way, the same component (vertical or horizontal as the case may be) became brighter than the other for all the wave-lengths. This clearly shows that benzene does not exhibit any appreciable dispersion of depolarisation. The depolarisation factor  $\rho_u$  calculated from the nicol reading for which the two components are equal in intensity is given in Table I.

In the case of formic acid it was found that for a particular orientation of the nicol, the two components were equal in intensity for  $\lambda$  2536 A.U., whereas the vertical component was still brighter than the horizontal component for  $\lambda$  4358 A.U. Conversely for another orientation of the nicol when the two components were equal in intensity for  $\lambda$  4358 A.U., the horizontal component was brighter than the vertical component for  $\lambda$  2536 A.U. For an intermediate position of the nicol the vertical component for  $\lambda$  4358 was brighter than the horizontal component, whereas for  $\lambda$  2536 the horizontal component was brighter than the vertical component. The values of  $\rho_u$  for different wave-lengths are given in Table I.

Acetic acid also exhibited a similar phenomenon. In this case it was noticed that when the nicol was so orientated as to equalise in intensity the two components for  $\lambda$  2536 the horizontal component for  $\lambda$  4358 was still brighter than the vertical component. Again when the nicol was rotated further so as to equalise in intensity the components for  $\lambda$  4358 the vertical component for  $\lambda$  2536 was brighter than the horizontal component. This shows that acetic acid exhibits a dispersion of depolarisation but in the opposite direction. The values of  $\rho_u$  for different wave-lengths are given in Table I. In propionic acid also an appreciable dispersion of depolarisation was observed. Normal butyric acid did not transmit the ultra-violet region and exhibited a strong fluorescence in the visible region. Consequently no quantitative measurement of depolarisation was made. Isobutyric acid also strongly absorbed the ultra-violet region. But it did not show any appreciable fluorescence in the visible region.

TABLE I.

$\lambda$ in A. U.	4358 $\rho_u$ %	4046 $\rho_u$ %	3650 $\rho_u$ %	2967 $\rho_u$ %	2536 $\rho_u$ %
1. Benzene ..	45.5	45.5	45.5	45.5	absorbed
2. Formic acid ..	47	47	49	50.8	52.8
3. Acetic acid ..	44	44	42.2	40.5	36
4. Propionic acid ..	42	42	43.7	44	absorbed
5. Isobutyric acid ..	36	36	36	absorbed	absorbed

## 4. Theoretical Discussion.

It is well known that the depolarisation factor of the light scattered by the molecules in the gaseous state is a measure of their optical anisotropy, in other words, is due to the fact that the optical polarisabilities of the molecules are different in different directions. K. R. Ramanathan<sup>6</sup> has derived a formula for the depolarisation of the light scattered transversely by the molecules in the fluid state given by the following expression:—

$$\rho_u = \frac{6\delta}{\frac{5RT\beta n}{N} + 7\delta} \quad \dots \quad (1)$$

where  $\rho_u$  = depolarisation factor when the incident light is unpolarised.

R = gas constant.

T = absolute temperature.

$\beta$  = compressibility coefficient.

$n$  and  $N$  are the number of molecules per c.c. and per gram molecule of the fluid.

$\delta$  is what is called the anisotropy factor and it is given by

$$\delta = \frac{A^2 + B^2 + C^2 - AB - BC - CA}{(A + B + C)^2} \quad \dots \quad (2)$$

where A, B and C are the optical moments induced in the molecule when it is placed in a field of unit intensity respectively along its three principal axes. For gases and vapours at low pressures which obey Boyle's law to a

first approximation  $\frac{RT\beta n}{N} = 1$  and consequently  $\rho_u = \frac{6\delta}{5 + 7\delta} \quad \dots \quad (3)$

<sup>6</sup> K. R. Ramanathan, *Ind. Jour. Phys.*, 1927, 1, 420.

It follows from equations 2 and 3 that if the ratio of the polarisabilities along any two axes in the molecule depends on the wave-length of the incident light wave, the optical anisotropy as well as the depolarisation factor will vary with the wave-length. Such a dispersion of optical anisotropy would be a genuine molecular property. On the other hand, if the ratio of the polarisabilities is independent of wave-length, the depolarisation factor also will be independent of wave-length.

In the case of a non-associated liquid, the depolarisation factor  $\rho_u$  is given by the same equation 1 (given above). But the value of  $\delta$  is given by the following<sup>7</sup> :

$$\delta = \frac{(A' - B')^2 + (B' - C')^2 + (C' - A')^2}{2(A' + B' + C')^2} \quad \dots \quad (4)$$

where  $A' = A(1 + p_1 \chi)$

$B' = B(1 + p_2 \chi)$

$C' = C(1 + p_3 \chi)$

$p_1$ ,  $p_2$  and  $p_3$  are the constants of anisotropy of the polarisation field.  $\chi$  is the susceptibility of the medium. In the case of ordinary liquids also, if the anisotropy factor depends on the wave-length of the incident light wave, the depolarisation factor will show a dispersion. From a comparison of the expressions for  $\rho_u$  in the liquid state and in the state of vapour, it is seen that if the molecules in the vapour state do not exhibit any dispersion, no dispersion will be exhibited by them in the liquid state. On the other hand, if they show an appreciable dispersion in the gaseous state they may show a dispersion in the liquid state as well but to a much smaller degree.

The generalisations given above are not applicable to the case of highly associated liquids, such as liquid fatty acids. S. Ramachandra Rao<sup>8</sup> has studied the variations of intensity and depolarisation factor of the transversely scattered light in the case of a large number of liquids. He finds that in almost all liquids the optical anisotropy as calculated from the depolarisation values increases with rise in temperature. But in acetic acid the anisotropy decreases when the temperature is raised up to 120° C. and above that temperature, it increases in the normal way.

Very recently the variations in intensity and depolarisation factor of the transversely scattered light have been studied by the author<sup>9</sup> in the case of the first four fatty acids with the incident light in the three different states of polarisation, namely unpolarised, horizontally polarised and vertically

<sup>7</sup> C. V. Raman and K. S. Krishnan, *Phil. Mag.*, 1928, 5, 498.

<sup>8</sup> S. Ramachandra Rao, *Indian Journal of Physics*, 1928, 3, 1.

<sup>9</sup> R. S. Krishnan, *Proc. Ind. Acad. Sci.*, A, 1936, 3, 126.

polarised. In the case of formic acid and acetic acid the depolarisation factor  $\rho_h$  is found to be distinctly less than 1, contrary to the molecular theory of light scattering.  $\rho_h$  increases with rise in temperature attaining its limiting value of unity at about 90° C. The intensity of scattering also at first diminishes with rise in temperature in these liquids. These observations have furnished for the first time definite experimental evidence for the existence of large molecular aggregates in these highly associated liquids of size not small compared with the wave-length of light. In these highly associated liquids, the depolarisation factor  $\rho_u$  arises not only from the actual anisotropy of the individual scattering particles, but also from their finite size. The depolarisation factor arising from the finite size of the molecular groups will increase with decrease of wave-length. Therefore it is natural to expect an appreciable dispersion of depolarisation. The increase of depolarisation with diminution in wave-length in the case of formic and propionic acids can very easily be explained on the basis of association. In formic acid since the association is greater, the dispersion is also greater than in propionic acid. But it remains unexplained why in the case of acetic acid the depolarisation factor diminishes as the wave-length decreases.

In conclusion the author takes this opportunity to express his grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his kind interest in the work.

#### 5. Summary.

The paper describes the results of measurements on the dispersion of polarisation of light scattered by benzene, formic acid, acetic acid, propionic acid and isobutyric acid. The depolarisation factor for benzene is constant over a wide range of wave-length. In the case of formic acid and propionic acid the depolarisation factor is found to increase and in acetic acid it is found to decrease as we proceed towards the ultra-violet. It is pointed out that the formation of large molecular groups in the fatty acids is probably responsible for the observed dispersion of depolarisation.