23. *Molecular Polarisability. The Photoelectrical Measurement of Depolarisation Factors: The Determination of $_{\infty}\delta_2^2$ for Six Alcohols in Carbon Tetrachloride.*

By R. J. W. LE FÈVRE and B. PURNACHANDRA RAO.

Depolarisation factors Δ for the light scattered transversely by liquids can be satisfactorily obtained by using a photometer containing an electron multiplier to measure directly the intensities of the horizontally and vertically polarised components. Experimental arrangements and their checking are described. If the multiplier output currents, proportional to the intensities, are i_h and i_v respectively, then $\Delta = i_h/i_v$. Data for a number of substances and for six normal alcohols dissolved in carbon tetrachloride are recorded. The technique has advantages over the older Cornu method.

DEPOLARISATION factors previously reported[1-4] from these laboratories have been determined by the Cornu method in which two images of the scattering track, viewed through a Wollaston prism–Nicol prism combination, are equalised in intensity by rotation of the Nicol prism. Experience has shown that, as a routine adjunct to Kerr-effect studies, the technique has disadvantages. The feebleness of the illuminations to be matched makes eye fatigue rapid and necessitates a long preliminary period of dark adaptation for the observer. The object of the present work was to increase both speed and objectivity by using photoelectric in place of visual detection.

Choice and testing of apparatus was the initial problem. Anantha Krishnan[5] and Kudryavtzeva[6] seem to be two of the earliest investigators to have attempted the application of photoelectric cells to light-scattering experiments; the former used an ordinary gas-filled photocell in conjunction with a valve bridge amplifier. He specifically alludes to the possibility of using this technique for the determination of the depolarisation factors of substances. With the marketing of multiplier phototubes (such as R.C.A. 931, IP21, or E.M.I. tubes, etc.) the opportunities for photoelectric photometry were greatly increased; papers by, *e.g.*, James and Glover,[7] Rank,[8], Debye,[9] Doty,[10] Hadow,[11] and Zimm[12] may be cited. These workers were mainly concerned with the turbidities of dilute polymer solutions, but Hadow and Rank also reported depolarisation factors for benzene and a few other pure liquids; inconstancy of the light source was evidently troublesome, and was avoided only by adding instrumental complexities such as monitoring systems involving potentiometric balancing,[12] or defocusing of the electron beam in the multiplier.[11]

EXPERIMENTAL

Present Apparatus.—Our preliminary experiments showed that an ordinary 6-volt car head-lamp bulb fed from a large storage battery formed a satisfactorily steady input source when used in conjunction with an E.M.I. 6260B multiplier phototube. This tube combines high cathode sensitivity, large cathode area, high magnification, and small dark current. The large cathode area is especially advantageous since in manufacture the achievement of cathode uniformity is made easier during the activation process; moreover, it permits the use of a

---

[1] Le Fèvre and Rao, *J.*, 1957, 3644; 1958, 1465.
[2] Le Fèvre, Le Fèvre, Rao, and Smith, *J.*, 1959, 1188.
[3] Bramley, Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 1183.
[4] Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 2340.
[5] Anantha Krishnan, *Proc. Ind. Acad. Sci.*, 1934—35, **1**, 201.
[6] Kudryavtzeva, *Acta Physicochim. U.R.S.S.*, 1935, **3**, 613.
[7] James and Glover, *R.C.A. Review*, 1941, **6**, 43.
[8] Rank *et al.*, *J. Opt. Soc. Amer.*, 1942, **32**, 390; 1943, **33**, 31; 1946, **36**, 325; 1947, **37**, 798.
[9] Debye, *J. Appl. Phys.*, 1944, **15**, 338; 1946, **17**, 392; *J. Phys. Colloid Chem.*, 1947, **51**, 18.
[10] Doty, Wagner, and Singer, *J. Phys. Colloid Chem.*, 1947, **51**, 32.
[11] Hadow, Sheffer, and Hyde, *Canad. J. Res.*, 1949, *B*, **27**, 791.
[12] Zimm, *J. Chem. Phys.*, 1948, **16**, 1099.

broad and slightly diffused light beam, so that the scattered radiation from the sample cell, after passing through an appropriately oriented Nicol prism, can be made to strike the photocathode without needing to be condensed into a spot of light. In fact, such condensation is best avoided since it may cause rapid local fatiguing, and non-linearity in response (cf. refs. 11 and 12).

The tube is mounted horizontally as follows: Its insulated base socket A is held in a brass collar B which is attached by three rods to a circular plate C through the centre of which two leads pass *via* light-tight ceramic bushes. The rods are of sufficient length to permit the necessary resistors to be soldered between the legs of the phototube D and yet to be safely clear of B and C. A brass ring E, shaped appropriately, fits over the head of D and is held in position by two springs linking it to B; in addition to holding the tube taut, E also forms the cathode connection, which for this tube is at the top; E is earthed. The assembly on C is screwed into a long, internally blackened, brass container F which is closed at the other end except for a circular aperture of *ca.* 1 in. diameter; component F, besides housing the photomultiplier, shields it from external electrical disturbances. Attached over the aperture is a disc G carrying a projecting tube H which slips into a corresponding tube on the holder of the rotatable Nicol prism; a shutter with a variable diaphragm is installed between G and H.

The phototube used had eleven multiplying stages; under an interdynode voltage of 160 v its minimum dark current was 10^{-14} A and its overall gain at least 10^7. An electronically stabilised power supply, of the conventional oscillator–E.H.T. rectifier–feed-back amplifier type, formed the primary voltage source. Optical arrangements, other than those mentioned above, were the same as with the Cornu method.[1] Output currents, caused by scattered light, were read as increased deflections in a sensitive galvanometer, connected between the positive terminal of the high-tension unit and the anode of the multiplier, observed when the shutter between G and H was opened.

The assembly in F is mounted on an optical bench, the Nicol prism holder inserted, and the whole then brought against one wall of a small, glass, cubical water-bath. The last-named is blackened internally, three 1 cm. diameter transparent circles, two for the transmitted beam and one for the scattered rays, being left on three faces. The spherical Pyrex sample-containing flasks, also blackened except for three windows to correspond with those in the bath, are held by the lid of the water-bath. Deflections are recorded for the Nicol prism alternately oriented to pass the horizontally and vertically polarised light; their ratio is nearly the depolarisation factor Δ sought: $\Delta =$ (intensity of horizontally polarised component) $\div$ (intensity of vertically polarised component).

A cause of inaccuracy is the presence of a small amount of background illumination, to minimise which the experimental cell is immersed in water: it may come from secondary scattering by the liquid in the cell, from reflections at the light entrance and exit points, etc. Such extra light is less polarised than the primary scattered beam so that the apparent Δ, especially if Δ is small, may be erroneously large. Suppose B_h and S_h, and B_v and S_v, are the intensities of the horizontal and vertical components of the background (B) and primary (S) scattering respectively; then in one position of the Nicol prism B_h and S_h are transmitted, and in the other B_v and S_v. Accordingly, the apparent depolarisation factor Δ' is $\Delta' = (B_h + S_h)/(B_v + S_v)$, but the B_v component is generally very small in comparison with S_v and hence can be neglected; Δ' is therefore $(S_h/S_v) + (B_h/S_v)$, of which the former term is the true Δ for the substance, *i.e.*, $\Delta = \Delta' - (B_h/S_v)$. For this reason the standard procedure adopted is the following: Deflections corresponding to Δ' are first recorded; then the cell plus sample is rotated by 180° so that no window in it now faces the observation aperture of the water-bath. In this position the incident light still passes through the cell but only the diffused background illumination from the bath, flask exterior, etc., should reach the phototube. The galvanometer deflection due to B_h is noted, and the correction B_h/S_v readily obtained.

DISCUSSION

Justification of Method.—Chloroform, benzene, n-hexane, and carbon disulphide were first examined. These liquids were pure and dry; they were finally distilled in a closed system and collected directly in the experimental cell (cf. ref. 1). The size of the variable diaphragm in front of the phototube was manipulated to suit the intensity of the scattered beam, the idea being to use smaller apertures for intense scattering, as with carbon disulphide, and *vice versa.* Results are shown in Table 1 and agree reasonably with values in the literature,[13,14] determined by the visual (Cornu) method.

Similar experiments with carbon tetrachloride next received considerable attention because this is our standard solvent for Kerr-effect studies. Rank [8] in 1947, using an R.C.A. IP21 multiplier, noted 100Δ as 10·0. Twelve sets of ratios of galvanometer deflections, taken on different days, were recorded for independently purified samples; 100Δ consistently lay between the extremes 4·27 and 4·35, with an average of 4·32 and a standard error of $\pm 0{\cdot}01$. This is slightly higher than that (3·46) previously found (and now repeated and checked) by the Cornu method. Attempts to ascertain the cause of the discrepancy have been unsuccessful. Consequently, we have used $\Delta_1 = 0{\cdot}0432$, when differences $\Delta\Delta_{12}$ between the depolarisation factors of several solutions and that of their solvent are being measured photoelectrically, but thenceforward in the calculations of ${}_{\infty}\delta_2{}^2$ we have proceeded, as in ref. 1, with $\Delta_1 = 0{\cdot}0346$. The effects of this procedure on ${}_{\infty}\delta_2{}^2$ were gauged by examining a number of solutes for which ${}_{\infty}\delta_2{}^2$ was known. The case of benzene–carbon tetrachloride is cited as an example:

TABLE 1. *Depolarisation factors obtained using a photomultiplier.*

Liquid	No. of detns.*	Max. and min. 100Δ found	Average 100Δ	Standard error (%)	100Δ by Cornu method †
Chloroform	6	22·19—22·60	22·40	±0·12	24·20
Benzene	6	40·82—42·92	41·50	±0·34	42·00
Hexane	5	9·55— 9·92	9·73	±0·41	9·95
Carbon disulphide	6	60·06—62·87	60·90	±0·51	62·00

* Each "determination" is itself an average of a large number of ratios of galvanometer deflections.

† Quoted from Table XI of Bhagavantam (ref. 14); Cabannes (ref. 14, pp. 181—187) cites a range of data in each case: chloroform, 15·0—24·2; benzene, 39·8—48·5; hexane, 9·9—10·0; carbon disulphide, 64·0—70·4. The following values of 100Δ have been recorded photoelectrically: benzene, 42·00—44·00 (Hadow *et al.*[11]), 39·00 (Rank, ref. 8, 1947), chloroform, 30·00 (Rank [8]), carbon disulphide, 54·00 (Rank [8]).

$10^5 f_2$	3093	6345	9327	11,708	15,873
$10^2\Delta_{12}$	$5{\cdot}98_4$	$8{\cdot}09_7$	$10{\cdot}0_1$	$11{\cdot}8_1$	$13{\cdot}1_2$

By least squares, $\Delta\Delta_{12} = 0{\cdot}6655 f_2 - 0{\cdot}603 f_2{}^2$; taking $(M_1 - M_2)/M_1$ as 0·49, D/d_1 as $-0{\cdot}38$, and $\delta_1{}^2$ as $1{\cdot}569 \times 10^{-3}$, we deduce (by eqn. 13 of ref. 1) that ${}_{\infty}\delta_2{}^2 = 33{\cdot}1_8 \times 10^{-3}$, a value comparing adequately with $32{\cdot}8 \times 10^{-3}$ earlier found by the Cornu method for benzene at infinite dilution. Similarly satisfactory results came from the other mixtures.

Finally, it is relevant that the direct observation of $\Delta\Delta_{12}$ as just described enables solutions to be prepared by filtration instead of by the time-consuming process of distillation without boiling, which in any case is impossible with many solid solutes. Solvent and solutions are separately allowed to percolate under gravity each in an apparatus consisting of an upper and lower vessel communicating *via* a sintered-glass plate (No. 4 pore size); a side-tube, also containing a small sintered disc, runs from just below the large disc to the upper part of the top unit, thus making possible filtration in a closed system without entry of air-borne dust. One of the experimental cells, attached by a standard glass joint, serves as the bottom receiver. This does not produce such optically "clean" liquids as does distillation, but experience and deliberate tests with volatile solutes have shown that *changes* of Δ from solvent to solutions are not significantly affected, and that values of ${}_{\infty}\delta_2{}^2$ so obtained are reliable.

Molecular Anisotropies of Alcohols.—The solutes were those used in the two preceding

---

[13] Bhagavantam, "Scattering of Light and the Raman Effect," Andhra Univ., Waltair, 1940.

[14] Cabannes, "La Diffusion Moléculaire de la Lumière," Les Presses Universitaires de France, Paris, 1929.

papers. Measurements were made photoelectrically and require no explanation except to say that, to avoid association, the concentrations were kept as low as possible. Tables 2 and 3 list the information needed for the calculation of the molecular anisotropies $_\infty\delta_2^2$ of the alcohols at infinite dilution.

Data exist in the literature for the first five alcohols both as vapours and as pure liquids. Because of association, $\delta_{2\text{liquid}}$ cannot be expected to be the same as either $_\infty\delta_2^2$ or δ^2_{vapour}. Table 6 of the next paper gives the values selected by Cabannes and Bhagavantum for inclusion in their monographs.

TABLE 2. *Depolarisation factors for light scattered by solutions of alcohols in carbon tetrachloride.*

10^5f_2	$10^2\Delta_{12}$	10^5f_2	$10^2\Delta_{12}$	10^5f_2	$10^2\Delta_{12}$	10^5f_2	$10^2\Delta_{12}$	10^5f_2	$10^2\Delta_{12}$	10^5f_2	$10^2\Delta_{12}$
0	4·320	0	4·320	0	4·320	0	4·320	0	4·320	0	4·320
Methyl		*Propyl*		*Pentyl*		*Ethyl*		*Butyl*		*Hexyl*	
2640	4·797	1408	4·528	1809	4·537	2182	4·682	1424	4·546	1492	4·454
3295	5·159	2525	4·667	2515	4·663	3006	4·800	2755	4·732	2699	4·621
4412	5·329	3959	4·872	4536	4·818	4458	5·000	4615	5·082	4223	4·861
4929	5·436	5374	5·073	8365	5·271	6737	5·329	6202	5·223	5425	5·028
		6322	5·125					7839	5·622	7616	5·253

TABLE 3. *Molecular anisotropies of alcohols at infinite solution in carbon tetrachloride.*

Solute alcohol	R.H.S. of equation giving $\Delta\Delta_{12}$	D/d_1 *	$\delta_2^2 \times 10^3$
Methyl	$0{\cdot}2027f_2 + 0{\cdot}574f_2^2$	$-0{\cdot}22$	$12{\cdot}0_5$
Ethyl	$0{\cdot}1673f_2 - 0{\cdot}268f_2^2$	$-0{\cdot}32$	$10{\cdot}0_7$
Propyl	$0{\cdot}1535f_2 - 0{\cdot}361f_2^2$	$-0{\cdot}40$	$9{\cdot}1_6$
Butyl	$0{\cdot}1447f_2 + 0{\cdot}219f_2^2$	$-0{\cdot}48$	$8{\cdot}4_7$
Pentyl	$0{\cdot}1227f_2 - 0{\cdot}117f_2^2$	$-0{\cdot}55$	$7{\cdot}1_9$
Hexyl	$0{\cdot}1194f_2 + 0{\cdot}077f_2^2$	$-0{\cdot}63$	$6{\cdot}7_6$

* $D = (d_{12} - d_1)/f_2$; values are calculated from the densities reported by Le Fèvre and Williams, *J.*, 1960, 108.

It is seen that in all cases $_\infty\delta_2^2$ is smaller than the reported anisotropy of the corresponding vapour; this resembles the type of difference previously[1] found for benzene or carbon disulphide or chloroform. However, no generalisations are possible, because in the instances just cited $_\infty\delta_2^2$ and δ^2_{liquid} are approximately equal, while here $_\infty\delta_2^2$ is roughly twice δ^2_{liquid}. A point of interest is that molecular anisotropy appears to diminish smoothly with increase of chain length only when the alcohols are in the liquid or the dissolved state. Further reference to the $_\infty\delta_2^2$'s of Table 3 will be made in the following paper.

We are grateful for a Research Scholarship from the Nuffield Foundation (to B. P. R.) for this and the following paper.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA.

[*Received, May* 1*st*, 1959.]