

721. Molecular Polarisability. The Determination of Molecular Anisotropy of Solutes from Scattering of Light by Solutions.

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

Depolarisation factors are measured for solutions in carbon tetrachloride of benzene, naphthalene, phenanthrene, carbon disulphide, chloroform, and acetone. A procedure is developed whereby the "molecular anisotropy" can be computed at infinite dilution. Values of ${}_{\infty}\delta_2^2$ so obtained are close to these found for the pure solutes, when these are liquids and when their isothermal compressibilities are available; the new method is advantageous in not requiring information on compressibilities (other than for the solvent) and in being applicable to solid compounds. For the calculation of semi-axes of polarisability from molar Kerr constants which have also been determined in solution, ${}_{\infty}\delta_2^2$ is shown to be more appropriate than δ_{gas}^2 . Previously-published data on b_1 , b_2 , and b_3 for chloroform and acetone are amended to 0.673, 0.901, 0.901 and 0.701, 0.684, and 0.482 (all $\times 10^{-23}$) respectively.

CALCULATION of the semi-axes, b_1 , b_2 , and b_3 , of a molecular polarisability ellipsoid in the general case where $b_1 \neq b_2 \neq b_3$ requires knowledge of at least three physical properties:¹ the molar Kerr constant (${}_mK$), the electronic polarisation (${}_EP$), and the molecular anisotropy (δ^2). Relevant equations are given as (1) to (3) (symbols have the meanings stated in ref. 1):

$${}_mK = 2\pi N(\theta_1 + \theta_2)/9 \quad \dots \quad (1)$$

$${}_EP = 4\pi N(b_1 + b_2 + b_3)/9 \quad \dots \quad (2)$$

$$\delta^2 = [(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]/(b_1 + b_2 + b_3)^2 \quad \dots \quad (3)$$

From the molar Kerr constant of a substance the sum ($\theta_1 + \theta_2$) of the "anisotropy" and the "dipole" terms respectively is obtained directly by eqn. (1); separation of θ_1 from θ_2 is effected through equations (2) and (3) to compute θ_1 :

$$\theta_1 = ({}_EP/45kT \cdot {}_EP)[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2] \quad \dots \quad (4)$$

θ_2 follows by difference:

$$\theta_2 = [(\mu_1^2 - \mu_2^2)(b_1 - b_2) + (\mu_2^2 - \mu_3^2)(b_2 - b_3) + (\mu_3^2 - \mu_1^2)(b_3 - b_1)]/45k^2T^2 \quad \dots \quad (5)$$

The desired semi-axes can then be evaluated from eqns. (2), (4), and (5). Relation (3) is thus of vital importance in all applications of the Kerr effect to problems of molecular structure.

The quantity δ^2 is drawn from experiment by eqn. (6):

$$\delta^2 = 10\Delta/(6 - 7\Delta) \quad \dots \quad (6)$$

where Δ is the "depolarisation factor" for light scattered transversely by the material when an unpolarised ray passes through it; Δ is defined as the ratio of the intensities of the light polarised in a horizontal plane (*i.e.*, the plane of the incident and scattered beams) to that polarised in a vertical plane.^{2,3} Actually eqn. (6) is valid only for scattering by gases. For liquids and dense media cognisance has to be taken of the fluctuations in the number of molecules in an element of volume V ; these are given by $(\overline{\Delta v})^2 = RT\beta v^2/NV$, where $(\overline{\Delta v})^2$ is the mean square of the deviation of the number of molecules per unit volume

¹ Le Fèvre and Le Fèvre, *J.*, 1953, 4041, 1954, 1577; *Rev. Pure Appl. Chem.*, 1955, 5, 261.

² Cabannes, "La Diffusion Moléculaire de la Lumière," Les Preoses Universitaires de France, Paris, 1929.

³ Bhagavantam, "Scattering of Light and the Raman Effect," Andhra University, Waltair, 1940.

from the mean value ν ; β is the isothermal compressibility. Consequently, for liquids, eqn. (7) should be used instead of (6):

$$\delta^2 = 10RT\beta\nu\Delta/(6 - 7\Delta)N \quad \dots \quad (7)$$

Unfortunately the literature contains depolarisation data for only a few dozen compounds. When the same substance has been examined in the liquid and the vapour state, δ^2 from (7), with use of $\Delta_{\text{liq.}}$ and β , and δ^2 from (6), with use of $\Delta_{\text{gas.}}$, have usually^{2,3} not been the same, $\delta_{\text{gas.}}^2$ always exceeding $\delta_{\text{liq.}}^2$.

Since we are using extensively molar Kerr constants $\infty_{(m)K_2}$ determined at infinite dilution in carbon tetrachloride and other solvents, and because many interesting substances are ordinarily solid and information on the isothermal compressibility of their melts is wholly lacking, the present work was initiated to enquire (a) whether δ^2 for a solute can be obtained directly from observations on a series of solutions, and (b) which, of $\delta_{\text{gas.}}^2$ or $\delta_{\text{liq.}}^2$, is the more appropriate for the calculation of θ_1 in $\infty_{(m)K_2}$.

EXPERIMENTAL

Depolarisation factors Δ were measured at *ca.* 20° by the Cornu method.^{2,3} Light from a 1000 w projection lamp was condensed on a 2 × 2 mm. square opening, acting as a source, situated close to the focus of a variable-aperture camera lens (*f* = *ca.* 30 cm.), mounted on the wall of a dark cabin inside which was an optical bench carrying a 50 c.c. spherical flask serving as the cell (this was painted black externally save for three small clear circles of *ca.* 1 cm. diameter for the incident and scattered beams), a Wollaston double-image prism, and a Nicol prism and circular scale readable to 0.01°. Mixtures were prepared by weight and concentrations recorded as molar fractions, f_2 . Freedom from dust and other particles was secured by distillation as described in refs. 1 and 2 or by filtration through sintered-glass diaphragms. The latter method was particularly explored because it was the only technique which could be applied to solutions of solid solutes; it did not produce such clear liquids as did the former, but provided that the solvent was similarly treated the changes in Δ from solvent to solutions were not significantly affected. The last point, which is essential to what follows, was exhaustively checked by experiments on systems in which both solvent and solute were easily volatile so that both methods could be used. In cases where fluorescence was suspected the incident light was first passed through aqueous quinine sulphate (3.6 g./100 c.c.) slightly acidified with sulphuric acid. Convergence corrections and other practical details were as described by Bhagavantam.³ If the two images seen through the Nicol-Wollaston combination were equally illuminated when the analyser made an angle ϕ with the horizontal, then $\Delta =$ (intensity of horizontally polarised component) ÷ (intensity of vertically polarised component) = $\tan^2 \phi$. Inversion of the Wollaston prism did not affect the readings of ϕ (cf. Volkmann⁴).

Carbon tetrachloride, used as solvent, was from a sulphur-free bulk supply which had been fractionated through a 1 m. column packed with glass helices. It was stored over calcium chloride and redistilled immediately before use. The solutes were purified by distillation or recrystallisation as appropriate.

Results.—The apparatus and technique were checked by making a number of determinations on five samples of redistilled sodium-dried benzene. Values of 100Δ fell between 40.1 and 41.0 (mean 40.6) with a standard error of ± 0.2 . Such a figure compares satisfactorily with others.^{2,3} In the case of carbon tetrachloride, purified as in the previous paragraph, however, 100Δ has been consistently found to lie within the limits 3.29 and 3.52, *i.e.*, lower than any earlier results (Cabannes² cites 4.45, 5.6, 6.1, 10.6, and 11.0 from various authors; Bhagavantam³ gives 6.0). It is possible that this difference can be explained by improvements, especially in distillation, introduced during the past 20 years in large-scale industrial manufacture, since older specimens and samples of "technical" grade have been found to give values of 100Δ of the order of those in the literature. For the material used in this work a mean value of $10^2\Delta_1 = 3.46 \pm 0.04$, from five separate preparations, was adopted.

Table I lists the depolarisation factors measured for solutions of six solutes in carbon tetrachloride. Subscripts 1, 2, and 12 denote solvent, solute, and solution respectively.

⁴ Volkmann, *Ann. Physik*, 1935, **24**, 457.

Molecular Anisotropy at Infinite Dilution.—Depolarisation factors of binary mixtures have been reported before,^{5, 6, 7} but never with the present objective of obtaining the molecular anisotropy of a solute at infinite dilution, $_{\infty}\delta_2^2$. The procedure now adopted may be outlined as follows: Equation (7) is rewritten for a solution containing a molar fraction f_2 of solute of molecular weight M_2 in a solvent of molecular weight M_1 :

$$\delta_{12}^2 = 10\Delta_{12}RT\beta_{12}d_{12}/(6 - 7\Delta_{12})M_{12} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $R = 0.8314 \times 10^8$ ergs/deg., T is the absolute temperature, and d is the density. The experimental values of Δ_{12} in Table I when plotted against f_2 form smooth curves which, near

TABLE I. *Depolarisation factors for solutes in carbon tetrachloride.*

Benzene		C ₁₀ H ₈		Phenanthrene		CS ₂		CHCl ₃		Me ₂ CO	
10 ⁵ f ₂	10 ² Δ ₁₂	10 ⁵ f ₂	10 ² Δ ₁₂	10 ⁵ f ₂	10 ² Δ ₁₂	10 ⁵ f ₂	10 ² Δ ₁₂	10 ⁵ f ₂	10 ² Δ ₁₂	10 ⁵ f ₂	10 ² Δ ₁₂
4742	6.30	1331	5.49	533	4.566	2021	7.13	1853	4.03	2206	5.13
9816	9.48	2134	6.73	1037	5.459	3686	12.34	3549	4.73	5755	5.99
13,993	13.44	3507	8.73	2042	6.863	6243	18.43	5144	5.51	9487	6.98
17,770	15.51	5022	10.03	2512	7.666	8336	22.21	7085	6.50	13,209	8.41
19,833	16.28			3877	10.470	10,774	30.59	9626	7.01	16,670	9.30
22,506	18.46					13,312	33.40	12,063	8.50	20,215	9.50
						16,181	38.55	15,040	9.70		
						20,783	39.91	19,287	12.56		

infinite dilution, can be taken as rectilinear (eqn. 9). A corresponding treatment has often been given⁸ to densities (eqn. 10); a similar relation will be assumed for the compressibility of a solution (eqn. 11).

$$\Delta_{12} = \Delta_1 + Af_2 \quad . \quad . \quad . \quad (9) \qquad \beta_{12} = \beta_1 + Bf_2 \quad . \quad . \quad . \quad (11)$$

$$d_{12} = d_1 + Df_2 \quad . \quad . \quad . \quad (10) \qquad M_{12} = M_1f_1 + M_2f_2 \quad . \quad (12)$$

Equation (8) is expanded, by substitution from equations (9) to (12), and differentiated with respect to f_2 . When $f_2 = 0$ equation (13) is obtained.

$$_{\infty}\delta_2^2 = \delta_1^2 \left[1 + \frac{A}{\Delta_1} + \frac{B}{\beta_1} + \frac{D}{d_1} + \frac{(M_1 - M_2)}{M_1} + \frac{7A}{(6 - 7\Delta_1)} \right] \quad . \quad . \quad . \quad (13)$$

In practice, equation (9) is not used as such, but values of $\Delta\Delta_{12} = \Delta_{12} - \Delta_1$ are fitted by least squares to (14), whence A follows as the coefficient of f_2 .

$$(\Delta\Delta_{12})f_2 = Af_2 + (\text{constant})f_2^2 \quad . \quad . \quad . \quad . \quad . \quad (14)$$

D can also be found by an expression analogous to (14); often it is adequately computed by eqn. (15):

$$D = \Sigma(\Delta d)/\Sigma f_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The constant B in an equation of type (11) presents some difficulty since unfortunately isothermal compressibilities of solutions as functions of concentration seem to have been little studied. An idea of the order of magnitude of B is obtained from the β 's for pure liquids published by Freyer, Hubbard, and Andrews;⁹ B should be roughly $\beta_2 - \beta_1$, e.g., for the system benzene-carbon tetrachloride, ca. -9.7×10^{-12} , so that $B/\beta_1 = -9.7/103.4 = \sim 0.094$. Parthasarathy¹⁰ has examined the adiabatic compressibilities of a few mixtures, including that just mentioned; from his results $(\beta_{12} - \beta_1)_{\text{adiab.}}/f_2\beta_1 = -0.046$. By either estimate B/β_1 is small, and, especially in view of the magnitudes of A/Δ_1 which enter (13), may safely be ignored.

Table 2 lists information, from Table 1, leading to $_{\infty}\delta_2^2$ for the various solutes in carbon tetrachloride, δ_1^2 for which is 1.569×10^{-3} at 20°, when d_1^{20} is 1.5940 and β_1 is 103.43×10^{-12} .

⁵ Rav, *Proc. Indian Ass. Cultivation Sci.*, 1925, **9**, 19.

⁶ Parthasarathy, *Indian J. Phys.*, 1934, **8**, 275.

⁷ Kremann and Gastinger, *Akad. Wiss. Wien*, 1938, **2**, B, **147**, 52.

⁸ Le Fevre, "Dipole Moments," Methuen, London, 3rd edn., 1953, p. 56.

⁹ Freyer, Hubbard, and Andrews, *J. Amer. Chem. Soc.*, 1929, **51**, 759.

¹⁰ Parthasarathy, *Proc. Indian Acad. Sci.*, 1936, **3**, 297.

Discussion.—Benzene and the last three compounds in Table 2 have been studied in both the liquid and the vapour state by several previous workers (see refs. 2 and 3). In Table 3 values of $\delta_{\text{liq.}}^2$ and δ_{gas}^2 , taken from refs. 2 and 3, and multiplied by 2 to conform to equations (6), (7), (8), and (13), are compared with ${}_{\infty}\delta_2^2$ now found. It is seen that

TABLE 2. Calculation of molecular anisotropies of solutes at infinite dilution.

Solute	Right-hand side of eqn. (14)	<i>D</i>	$10^3 {}_{\infty}\delta_2^2$
Benzene	$0.657f_2 + 0.046f_2^2$	-0.5997	32.8
Naphthalene	$1.686f_2 - 7.07f_2^2$	-0.6749	80.9
Phenanthrene	$1.666f_2 + 3.05f_2^2$	-0.6671	79.4
Carbon disulphide	$2.879f_2 - 5.08f_2^2$	-0.4286	137.9
Chloroform	$0.332f_2 + 0.680f_2^2$	-0.0899	17.5
Acetone	$0.502f_2 - 0.989f_2^2$	-0.6285	25.6

TABLE 3. Values of $\delta_{\text{liq.}}^2$, δ_{gas}^2 , and ${}_{\infty}\delta_2^2$.

	$10^3 \delta_{\text{liq.}}^2$	$10^3 \delta_{\text{gas}}^2$	$10^3 {}_{\infty}\delta_2^2$
Benzene	36.0	79.2	32.8
Carbon disulphide	145	221	138
Chloroform	18.6	30.6	17.5
Acetone	25.4	27.3	25.6

equation (13) leads to molecular anisotropies which are close to those calculated from $\Delta_{\text{liq.}}$, $\beta_{\text{isothermal}}$, etc. Eqn. (13) therefore offers the practical advantage that ${}_{\infty}\delta_2^2$ becomes accessible for the many solid and other substances for which isothermal compressibilities are unknown.

There remains the question which, of ${}_{\infty}\delta_2^2$ (or $\delta_{\text{liq.}}^2$) or δ_{gas}^2 , is the more appropriate for use in calculating θ_1 from a molar Kerr constant determined at infinite dilution in a solvent. Table 4 gives the results of estimating δ^2 by equations (1), (2), and (3) in the

TABLE 4. Values of ${}_{\infty}\delta_2^2$ calculated from ${}_{\infty}(mK_2)$ and by eqn. (13).

Solute	$10^{12} {}_{\infty}(mK_2)$	ϵP (c.c.)	$10^3 {}_{\infty}\delta_2^2$ from ${}_{\infty}(mK_2)$	$10^3 {}_{\infty}\delta_2^2$ by eqn. (13)
Benzene	7.24 ^a	25.1 ^a	34.8	32.8
Naphthalene	48.1 ^b	41.8 ^b	85.7	80.9
Phenanthrene	82.6 ^c	56.9 ^d	72.2	79.4
Carbon disulphide	27.8 ^c	20.4 ^e	191	138

^a From ref. 1. ^b From ref. 11. ^c From unpublished work. ^d Estimated by taking $D_P/\epsilon P$ as 1.1. ^e From ref. 12.

cases of four non-polar solutes, for each of which $\theta_2 = 0$ in eqn. (1). With benzene, naphthalene, and phenanthrene it is clear that ${}_{\infty}\delta_2^2$ is adequate for the purpose mentioned. With carbon disulphide, an anisotropy about midway between ${}_{\infty}\delta_2^2$ or $\delta_{\text{liq.}}^2$ and δ_{gas}^2 seems to be required—a fact for which we have no explanation at present. Fortunately, in practice eqn. (13) will be needed during the extraction of b_1 , b_2 , and b_3 for a polar molecule, whose θ_2 is likely greatly to exceed θ_1 , so that high precision in θ_1 will not be essential (cf. pyridine and quinoline¹³).

TABLE 5. Values of δ^2 calculated from semi-axes already published.

Molecule	Ref.	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^3\delta_2^2$
Benzene	1	1.114	1.114	0.733	33.1
Naphthalene	11	2.15	1.76	1.03	79.5
Chloroform *	1	0.673	0.901	0.901	17.0

* The semi-axes for chloroform are incorrectly given in Tables 7 and 8 of *J.*, 1953, 4041. They should read as above with CCl_4 as solvent, and as 0.665, 0.904, 0.904 respectively with C_6H_6 as solvent.

Reference is made in Table 5 to three substances whose polarisability ellipsoids have been derived in past papers without recourse to depolarisation data. As a check values of

¹¹ Le Fèvre and Le Fèvre, *J.*, 1955, 1641.

¹² Le Fèvre and Rao, *Austral. J. Chem.*, 1954, 7, 135.

¹³ Le Fèvre and Le Fèvre, *J.*, 1955, 2750.

δ^2 are evaluated directly, by eqn. (3), from the semi-axes. Agreement is reassuring, especially for naphthalene since in this instance Le Fèvre and Le Fèvre¹¹ used refractive indices of the crystal to compute b_1 , b_2 , and b_3 .

Finally, the analysis of acetone, given in *J.*, 1953, 4041, involved δ_{gas}^2 . In view of the conclusions now reached a more appropriate figure is ${}_{\infty}\delta_2^2 = 0.0256$; when this is used the semi-axes, b_1 , b_2 , and b_3 appear as 0.701, 0.684, and 0.482 (all $\times 10^{-23}$) cm. respectively.

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

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