

SHORT COMMUNICATIONS

KERR CONSTANT-DISPERSION MEASUREMENTS ON CYCLOHEXANE

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Le Fèvre and Solomons¹ recorded the Kerr constants B_λ of carbon tetrachloride and benzene over the wavelength range 375–625 nm to make possible the use of these solvents in examining the anisotropic polarizabilities^{2,3} of coloured solutes. Since, however, unsuspected hydrogen bondings may occur between π -electrons of benzene and protons from a dissolved molecule,⁴ and/or because of the various risks of chemical changes when basic substances are studied in carbon tetrachloride, an additional and more inert medium became desirable. Cyclohexane seemed⁴ to be the least reactive of the liquids which are available in quantity and easily purified, but no information on the variation of its B constant with wavelength was in the literature; the present measurements were therefore made to fill this gap.

Experimental

Commercial cyclohexane (Laboratory reagent grade, Ajax Chemicals Ltd) was partly frozen. The liquid was decanted and the remelted solid dried and stored over bright sodium wire. The product had m.p. c. 6.05° , d_4^{20} 0.7782, n_D^{20} 1.4262, d_4^{25} 0.77389, n_D^{25} 1.4235, and b.p. 80.5 – 80.8° ; by g.l.c. it appeared as a single substance; no aromatic hydrocarbons could be detected in u.v. spectra. The density and refractive index agree with data listed by Timmermans.⁵

The apparatus described by Le Fèvre and Solomons¹ has been rebuilt in Macquarie University without significant modification and has been used for most of the measurements at wavelengths other than 589 nm. With basically similar equipment at Sydney University, R.K.P. has independently made 26 determinations of B_{589} for cyclohexane at 25° . The Kerr cells used in the two centres differed from one another in length, inter-electrode spacings, and thermostating arrangements. Each was calibrated frequently with benzene and carbon tetrachloride, the Kerr constants for which were taken¹ as 0.410×10^{-7} and 0.083×10^{-7} , respectively, at 25° and for a λ of 589 nm. Seven observations by R.J.W.LeF., made separately at Macquarie University, were harmonious with those by R.K.P. From the total of 33 estimates, $10^7 B_{589}^{25}$ for cyclohexane has emerged as 0.053 ± 0.001 , a value slightly less than any previously quoted by the Sydney

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¹ Le Fèvre, R. J. W., and Solomons, S. C., *Aust. J. Chem.*, 1968, **21**, 1703.

² Le Fèvre, R. J. W., *Adv. phys. org. Chem.*, 1965, **3**, 1.

³ Le Fèvre, R. J. W., *Rev. pure appl. Chem.*, 1970, **20**, 67.

⁴ Le Fèvre, R. J. W., Radford, D. V., Ritchie, G. L. D., and Stiles, P. J., *J. chem. Soc. (B)*, 1968, 148.

⁵ Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds." (Elsevier: New York 1950.)

group,^{4,6,7} Stuart,⁸ and Leiser.⁹ Data for other wavelengths, obtained by procedures outlined before,¹ are in Table 1.

Variation of B_λ and n_λ with λ

The Kerr constants in Table 1, when plotted against wavelengths, lie on a curve which rises towards the violet end of the range. As with carbon tetrachloride or benzene,¹ the graph of B_λ against $1/\lambda^2$ is rectilinear. Equation (1) is obtained by a least-squares fit:

$$B_\lambda(C_6H_{12}) = 0.0245 \times 10^{-7} + 10.299 \times 10^{-18}/\lambda^2 \quad (1)$$

Found and calculated values of B_λ are compared in Table 1.

TABLE 1

KERR CONSTANTS FOR CYCLOHEXANE AT 25° AND WAVELENGTHS BETWEEN 600 AND 375 nm
Wavelengths quoted are the maximum transmittances reported by the makers (Zeiss-Jena) of the metal interference filters used

λ (nm)	600	589 ^a	575	550	525	500	475	450	436	425	400	375
$10^{11}B_\lambda$ (obs.)	532	539	558	586	624	653	710	754	783	804	892	982
$10^{11}B_\lambda$ (calc.) ^b	531	542	556	585	619	657	701	754	787	815	889	978

^a See text regarding B_{589} .

^b Calculated by equation (1).

Timmermans⁵ quotes refractive indices of cyclohexane at 25° for the α -, β -, and γ -hydrogen and sodium-D lines; we find these data to be adequately covered by equation (2):

$$n_\lambda^2 = 1.99427 + 0.01120 \times 10^{-8}/\lambda^2 \quad (2)$$

In (1) and (2) λ is introduced as centimetres. Alternative expressions¹ incorporating both B_λ and n_λ are more complicated and do not encompass the observed B_λ or n_λ^2 values better than (1) or (2). The quotient $B_\lambda n_\lambda \lambda / (n_\lambda^2 - 1)^2$, which should be invariant with λ if Havelock's rule¹⁰ were obeyed, increases from 431×10^{-15} to 458×10^{-15} as λ is reduced from 600 to 375 nm. For these reasons the "smoothed" values of B_λ and n_λ , provided by (1) and (2), are used as a basis for Table 2.

Information Needed for the Measurement of Molar Kerr Constants in Cyclohexane

The molar Kerr constant ${}_m K_2$ of a solute at infinite dilution is evaluated¹ from observations on solutions having (weight fraction) concentrations w_2 by equation (3):

$${}_m K_2 = {}_s K_1 (1 - \beta + \gamma + \delta - H\gamma - J\alpha\epsilon_1) M_2 \quad (3)$$

⁶ Le Fèvre, R. J. W., Orr, B. J., and Ritchie, G. L. D., *J. chem. Soc. (B)*, 1966, 273.

⁷ Le Fèvre, C. G., and Le Fèvre, R. J. W., Ch. 36 in "Physical Methods of Organic Chemistry." (Ed. A. Weissberger.) 3rd Edn, p. 2459. (Interscience: New York 1960.)

⁸ Stuart, H. A., "Die Struktur des Freien Moleküls." (Springer: Berlin 1952); "Molekülstruktur." pp. 435, 436. (Springer: Berlin 1967.)

⁹ Leiser, R., *Abh. dt. Bunsen-Ges.*, 1910, No. 4, 1.

¹⁰ Havelock, T. H., *Proc. R. Soc.*, 1907, **80**, 28; *Phys. Rev.*, 1909, **28**, 136.

where d , n , and ϵ stand for density, refractive index, and dielectric constant; subscripts 1, 2, and 12 indicate solvent, solute, and solution respectively:

$$\begin{aligned}\beta &= (d_{12} - d_1)/d_1 w_2 & \delta &= (B_{12} - B_1)/B_1 w_2 \\ \gamma &= (n_{12} - n_1)/n_1 w_2 & \alpha\epsilon_1 &= (\epsilon_{12} - \epsilon_1)/w_2\end{aligned}$$

TABLE 2
VALUES OF REFRACTIVE INDICES AND SOLVENT CONSTANTS FOR CYCLOHEXANE AT 25° AND WAVELENGTHS BETWEEN 600 AND 375 nm

λ (nm)	n_λ	H_λ	$10^{14}({}_sK_1)_\lambda$	λ (nm)	n_λ	H_λ	$10^{14}({}_sK_1)_\lambda$
600	1.42316	2.0126	1.3425	475	1.42965	2.0217	1.3966
589	1.42357	2.0132	1.3448	450	1.43163	2.0245	1.4211
575	1.42412	2.0140	1.3462	436	1.43289	2.0262	1.4359
550	1.42523	2.0155	1.3538	425	1.43397	2.0277	1.4484
525	1.42650	2.0173	1.3661	400	1.43675	2.0316	1.4840
500	1.42796	2.0193	1.3795	375	1.44012	2.0362	1.5268

M_2 is the molecular weight of the solute; H , J , and ${}_sK_1$ are solvent constants given by (4)–(6):

$$H_\lambda = 4n_\lambda^2/(n_\lambda^2 + 2) \quad (4)$$

$$J = 2/(\epsilon + 2) \quad (5)$$

$$({}_sK_1)_\lambda = 6\lambda n_\lambda B_\lambda / (n_\lambda^2 + 2)^2 (\epsilon + 2)^2 d_1 \quad (6)$$

Table 2 sets out the values of H_λ and $({}_sK_1)_\lambda$ required for use in (3) at the wavelengths corresponding to the Zeiss-Jena metal interference filters available to us and specified on pp. 14–16 of the maker's pamphlet W 32-846a-2. At 25° the density is taken as 0.77389 g/cm³ and the dielectric constant¹¹ as 2.0199. (This ϵ is the highest on record,^{12–15} but does not exceed the least of the observed⁵ n_λ^2 values; nevertheless, total and electronic polarizations of 27.59 and 27.10 cm³ are calculable from present data, and an atomic polarization of the expected^{16,17} order is thereby indicated.) Interpolated values of B_λ , n_λ^2 , H_λ , and $({}_sK_1)_\lambda$ are accessible through equations (1), (2), (7), and (8):

$$H_\lambda = 1.9974 + 0.5462 \times 10^{-10}/\lambda^2 \quad (7)$$

$$10^{14}({}_sK_1)_\lambda = 1.2775 + 1.397 \times 10^{-10}/\lambda^2 + 0.30 \times 10^{-18}/\lambda^4 \quad (8)$$

At 25° J is 0.4975.

¹¹ Le Fèvre, R. J. W., *Trans. Faraday Soc.*, 1938, **34**, 1127.

¹² Maryott, A. A., and Smith, E. R., *Natn. Bur. Stand. Circ.* 514. (U.S. Department of Commerce: Washington 1951.)

¹³ Hooper, G. S., and Kraus, C. A., *J. Am. chem. Soc.*, 1934, **56**, 2265.

¹⁴ Dickinson, R. G., and Wood, R. E., *J. Am. chem. Soc.*, 1939, **61**, 3259.

¹⁵ Philippe, R., and Piette, A. M., *Bull. Soc. chim. Belg.*, 1955, **64**, 5, 600.

¹⁶ Le Fèvre, R. J. W., and Narayana Rao, D. A. A. S., *Aust. J. Chem.*, 1955, **8**, 39.

¹⁷ Le Fèvre, R. J. W., and Steel, K. D., *Chem. Ind.*, 1961, 670.