

113. Molecular Polarisability: Chlorobenzene as a Solvent for the Determination of Molar Kerr Constants of Solutes.

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The application is reported of standard procedures for the determination of dipole moments and molar Kerr constants to solutions of benzene, naphthalene, phenanthrene, carbon disulphide, carbon tetrachloride, or chloroform, in chlorobenzene. The apparent values of μ and ${}_mK$ thus secured are compared with others obtained previously in chloroform or carbon tetrachloride.

THE measurements here recorded have been made for the reasons set out by us in the first paragraph of ref. 1, in which we reported the limited usefulness of chloroform as a solvent in which to determine molar Kerr constants of solutes. Standard procedures are now applied to solutions in chlorobenzene of six substances for which data in benzene or carbon tetrachloride are already available. The apparent molar Kerr constants in the polar and non-polar media are then compared.

EXPERIMENTAL

Solutes and Solvent.—The former were recrystallised or redistilled as necessary. A bulk supply of chlorobenzene was prepared by washing commercial material with water until neutral, drying (CaCl_2), and fractionation (b. p. 131—132°/760 mm.).

Observations.—These are listed in Table 1 which gives: weight fractions w_2 of solutes, densities d_4^{25} and dielectric constants ϵ^{25} of solutions, and the differences Δn_D and ΔB between the refractive indexes and Kerr constants of solutions and solvent. Results are given in Tables 2 and 3. Apparatus, methods of calculation, definitions of symbols used, etc., have been fully explained before (cf. refs. 1, 3, 7, 8 cited by Le Fèvre and Williams¹).

The following constants apply to chlorobenzene at 25°:

d_1	1.1009	ϵ_1	5.612	B_1	12.42×10^{-7}	C	0.04703	H	2.146
n_1	1.5215	p_1	0.5503 _s	r_1	0.27684	D	0.14636	J	0.2628
				${}_sK_1$	0.5626×10^{-12}				

The value of ϵ_1 is from Sugden,² that of B_1 is deduced from the Kerr constant (3.85) relative to carbon disulphide.³

¹ Le Fèvre and Williams, *J.*, 1961, 1671.

² Sugden, *J.*, 1933, 768.

³ Mouton. "International Critical Tables," 1930, Vol. VII, p. 109.

TABLE I.

Kerr constants, refractivities, dielectric constants, and densities of solutions in chlorobenzene containing weight fractions w_2 of solute at 25°.

Solute: Benzene.							
$10^5 w_2$	4818	11,497	11,881	22,671	24,648	27,131	28,260
d_4^{25}	1.0884	—	—	1.0409	1.0350	1.0285	1.0255
ϵ^{25}	5.377	—	5.094	4.682	4.597	4.506	4.455
$10^4 \Delta n_D$	-11	-31	-33	-59	-65	-70	-75
$10^7 \Delta B$	-1.29	-1.76	-1.94	-3.30	-3.49	-3.70	-3.90
$10^5 w_2$	38,630	53,402	63,241	66,254	76,475	84,525	
d_4^{25}	1.0005	0.9660	0.9459	0.9392	0.9188	0.9030	
ϵ^{25}	4.082	3.585	3.269	3.185	2.883	2.655	
$10^4 \Delta n_D$	-102	-137	-158	-164	-187	-205	
$10^7 \Delta B$	-4.90	-6.30	-7.65	-7.92	-9.00	-10.27	

Whence $\Delta d = -(0.281 \pm 0.001)w_2 + 0.056w_2^2$; $\Delta \epsilon = -(4.138 \pm 0.007)w_2 + 0.80w_2^2$; $\Delta B = -(14.3 \pm 0.3)w_2 + 3.1w_2^2$; $\sum \Delta n / \sum w_2 = -0.0253$ (w_2 's taken between 0 and $84,525 \times 10^{-5}$); $\sum \Delta n / \sum w_2 = -0.0263$ (for w_2 between 0 and $28,260 \times 10^{-5}$).

Solute: Naphthalene.							
$10^5 w_2$...	3399	6424	6555	9901	11,004	14,690	17,020
d_4^{25}	1.0972	1.0950	1.0951	1.0922	1.0913	1.0883	1.0865
ϵ^{25}	5.454	5.358	5.355	5.249	5.216	5.101	5.026
$10^4 \Delta n_D$	+101	+196	+220	+315	+346	+447	+549
$10^7 \Delta B$...	-0.15	-0.30	-0.39	-0.45	-0.60	-0.98	-1.17

Whence $\sum \Delta d / \sum w_2 = -0.0871$; $\sum \Delta \epsilon / \sum w_2 = -3.150$; $\sum \Delta n / \sum w_2 = +0.1034$; $\sum \Delta B / \sum w_2 = -6.19$.

Solute: Phenanthrene.							
$10^5 w_2$...	5507	6517	9117	12,511	13,507	15,551	
d_4^{25}	1.1021	1.1023	1.1029	1.1037	1.1039	1.1042	
ϵ^{25}	5.420	5.395	5.322	5.238	5.202	5.148	
$10^4 \Delta n_D$	+96	+116	+159	+218	+237	+271	
$10^7 \Delta B$...	-0.44	-0.44	-0.81	-1.00	-1.00	-1.20	

Whence $\sum \Delta d / \sum w_2 = +0.0219$; $\sum \Delta \epsilon / \sum w_2 = -2.703$; $\sum \Delta n / \sum w_2 = +0.1750$; $\sum \Delta B / \sum w_2 = -7.93$.

Solute: Carbon disulphide.							
$10^5 w_2$...	1330	5498	11,140	13,947	18,710	21,220	33,156
d_4^{25}	1.1020	1.1071	1.1142	1.1175	1.1239	1.1272	1.1433
ϵ^{25}	5.540	5.432	5.282	5.210	5.076	5.005	4.668
$10^4 \Delta n_D$	+7	+33	+60	+91	+110	+143	+230

Whence $\sum \Delta d / \sum w_2 = +0.1237$; $\Delta \epsilon = -(2.560 \pm 0.005)w_2 - 0.52w_2^2$; $\sum \Delta n / \sum w_2 = +0.0646$.

$10^5 w_2$...	10,355	15,370	18,643	23,532	28,814
$10^7 \Delta B$...	-0.40	-0.59	-0.78	-1.18	-1.37

Whence $\sum \Delta B / \sum w_2 = -4.47$.

Solute: Carbon tetrachloride.							
$10^5 w_2$...	2427	3542	6361	10,323	12,192	14,801	21,422
d_4^{25}	1.1089	1.1125	1.1224	1.1363	1.1432	1.1526	1.1591
ϵ^{25}	5.521	5.491	5.432	5.336	5.293	5.223	5.176
$10^4 \Delta n_D$	-10	-13	-22	-41	-50	-58	-69
$10^7 \Delta B$...	-0.20	-0.57	-0.76	-0.96	-1.16	-1.36	-1.54

Whence $\sum \Delta d / \sum w_2 = +0.3558$; $\Delta \epsilon = -(2.10 \pm 0.01)w_2 - 1.34w_2^2$; $\sum \Delta n / \sum w_2 = -0.0415$; $\sum \Delta B / \sum w_2 = -9.30$.

Solute: Chloroform.							
$10^5 w_2$...	18,682	22,581	29,324	34,294	42,484	46,122	
d_4^{25}	1.1621	1.1960	1.2115	1.1736	1.2397	1.2523	
ϵ^{25}	5.503	5.484	5.447	5.421	5.373	5.355	
$10^4 \Delta n_D$	-108	-127	-182	-209	-280	-293	
$10^7 \Delta B$...	—	—	—	-4.18	-5.42	-6.02	
$10^5 w_2$...	60,058	70,578	78,699	90,800	95,604	100,000	
d_4^{25}	1.3034	1.3456	1.3808	1.4351	1.4576	1.4790	
ϵ^{25}	5.271	5.198	5.130	5.023	4.977	4.931	
$10^4 \Delta n_D$	-405	-498	-570	-696	-750	-796	
$10^7 \Delta B$...	-8.32	-9.89	-11.54	-13.59	-14.57	-15.60	

Whence $\Delta d = +(0.268 \pm 0.001)w_2 + 0.103w_2^2$; $\Delta \epsilon = -(0.353 \pm 0.006)w_2 - 0.289w_2^2$; $\sum \Delta n / \sum w_2 = -0.0713$; $\Delta B = -(10.8 \pm 0.3)w_2 + 4.71w_2^2$.

TABLE 2.

Total polarisations at infinite dilution, and apparent dipole moments, calculated from Table 1.

Solute	$(\alpha\epsilon_1)w_2=0$	$(\beta)w_2=0$	∞P_2 (c.c.)	R_D (c.c.)	μ (app.) (D)
Benzene	-4.138	-0.255	38.8	26.2*	0.78
Naphthalene	-3.150	-0.079	57.1	44.2	0.79
Phenanthrene	-2.70 ₂	+0.020	73.5	62.3	0.74
Carbon disulphide	-2.560	+0.112	28.0	20.9	0.59
Carbon tetrachloride	-2.10	+0.323	42.1	26.0	0.89
Chloroform	-0.353	+0.243	47.7	21.3	1.14

* Calc. from data for w_2 between 0 and 0.2826 in Table 1.

TABLE 3.

Molar Kerr constants and sums of anisotropy and dipole terms at infinite dilution calculated from Tables 1 and 2.

Solute	γ	δ	$10^{12} \infty (mK_2)$	$10^{25} (\theta_1 + \theta_2)$
Benzene	-0.0173	-1.148	+53.3	+12.7
Naphthalene	+0.0680	-0.50	+95.8	+22.8
Phenanthrene	+0.1150	-0.64	+96.1	+22.8
Carbon disulphide	+0.0424	-0.36	+49.3	+11.7
Carbon tetrachloride	-0.0273	-0.75	+44.3	+10.5
Chloroform	-0.0469	-0.87	+2.2 ₈	+0.5 ₄

DISCUSSION

Apparent Dipole Moments of Solutes.—These moments, for benzene, carbon disulphide, and chloroform, confirm the magnitudes of those earlier reported by Le Fèvre and Le Fèvre,⁴ and Le Fèvre and Russell:⁵

Solute	Apparent moments (D)	
Benzene	0.73 (ref. 4)	0.78 (present work)
Carbon disulphide	0.49 "	0.59 "
Chloroform	1.18 (ref. 5)	1.14 "

Holland and Le Fèvre⁶ wrote an empirical equation (involving shape factors of the solute and solvent molecules, and the molecular refractions of the former) by which apparent moments of normally non-polar species could be forecast in polar media; this when applied to the first five solutes of Table 2 yields the following:

Solute	C_6H_6	$C_{10}H_8$	$C_{14}H_{10}$	CS_2	CCl_4
App. μ calc.	0.68	0.85	0.95	0.60	0.72
" found	0.78	0.79	0.74	0.59	0.89

The agreement is satisfactory considering that the equation of ref. 6 was drawn from observations in two solvents only, and that the small apparent moments in Table 2 are themselves uncertain through being derived essentially from differences between much larger quantities, namely, the ∞P_2 's and R_D 's.

Apparent Molar Kerr Constants of Solutes.—Table 3 shows the mK 's in chlorobenzene to be algebraically more positive than those in carbon tetrachloride; in ref. 1 an opposite tendency was noted (except with naphthalene) when mK 's in chloroform and carbon tetrachloride were compared:

Solute	C_6H_6	$C_{10}H_8$	$C_{14}H_{10}$	CS_2	CCl_4	$CHCl_3$
$\infty (mK_2) \times 10^{12}$ in CCl_4	7.2	48.1	82.6	27.8	1.1	-28.5
" " $CHCl_3$	-5.2	51.4	71.0	17.0	-7.1	-17.6
" " $PhCl$	53.3	95.8	96.1	49.3	44.3	2.28

⁴ Le Fèvre and Le Fèvre, *J.*, 1936, 487.

⁵ Le Fèvre and Russell, *J.*, 1936, 491.

⁶ Holland and Le Fèvre, *J.*, 1950, 2166.

It thus appears that solutes in chlorobenzene undergo augmentation of moment more in directions inclined toward their greatest axes of polarisability than towards their least, and that for solutes in chloroform the reverse is true. At first sight the implication seems to be that solute and solvent molecules are not completely randomly arranged but that there is a tendency for associations to involve mutual orientations in which the largest and intermediate polarisability axes of both structures are situated in parallel planes, so that, *e.g.*, benzene in chloroform or chlorobenzene has its ring-plane parallel to the triangle of the three chlorine atoms of chloroform or to the ring-plane of chlorobenzene, respectively.

With such a model for the five "non-polar" solutes in chlorobenzene, estimates of their maximum polarisability semi-axes may be made from the data of Tables 2 and 3 by assuming that the apparent moments act along the said axes and that θ_1 is not much affected by the medium (*cf.* ref. 1); since the sums of the two smaller polarisabilities have in each case to be treated as a single unknown only the greatest b 's are thus accessible. Results emerge as follows:

Solute	$10^{25}\theta_1$	$10^{25}\theta_2$	Max. $10^{25}b$	Max. $10^{25}b$ in CCl_4	Ref.
Benzene	1.71	12.7	1.40	1.12	7
Naphthalene	11.4	22.8	2.22	2.15	8
Phenanthrene	19.6	22.8	2.62	(2.9?)	9
Carbon disulphide	6.61	11.7	1.20	1.31	10
„ tetrachloride	0.26	10.5	1.36	1.03	1

Chloroform has been omitted from the Table because, being itself dipolar, polarity induced in the plane of the chlorine atoms will cause the molecular resultant moment to act unpredictably in a direction between this plane and the H-C line; we note, however, that a moment of 1.14 D, acting at 25° to b_1 in the ellipsoid specified for chloroform by Le Fèvre and Rao,¹¹ would lead to a calculated molar Kerr constant ($+2 \times 10^{-12}$) resembling in sign and magnitude that now found in chlorobenzene.

Conclusion.—As an alternative solvent to carbon tetrachloride or benzene, chlorobenzene may have some applicability to non-polar solutes, a class for which chloroform seemed¹ unsuitable. However, in view of the speculative assumptions made above, it cannot be claimed that chlorobenzene is capable of providing, with certainty, quantitative information on the anisotropic polarisabilities of any type of solute.

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⁷ Aroney and Le Fèvre, *J.*, 1960, 360.

⁸ Le Fèvre and Le Fèvre, *J.*, 1955, 1641.

⁹ Le Fèvre and Sundaram, *J.*, 1963, 4442.

¹⁰ Armstrong, Aroney, Le Fèvre, Le Fèvre, and Smith, *J.*, 1958, 1474.

¹¹ Le Fèvre and Rao, *J.*, 1957, 3644.