325. *Molecular Polarisability. Chloroform as a Solvent for the Determination of Molar Kerr Constants of Solutes.*

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The apparent values of the molar Kerr constants and dipole moments of two polar, and five ordinarily non-polar, solutes in chloroform are reported and considered in relation to the corresponding data obtained in carbon tetrachloride. Results suggest that chloroform has a limited usefulness for the estimation of principal polarisabilities of strongly polar species such as chloro- and nitro-benzene, but with other solutes, such as benzene, naphthalene, carbon disulphide, etc., unavoidable experimental errors are evidently liable to introduce unpredictable uncertainties in the interpretation of measurements by our usual methods of calculation.

This work originated with the question: can useful measurements of molar Kerr constants be made in polar media? It became necessary because the applicability of molecular polarisability [1] to stereochemistry was obviously limited while only solutions in non-polar media could be examined, since many interesting compounds are insoluble in such liquids. Chloroform was selected for test because of its satisfactory solvent powers for a wide range of substances. Our plan therefore has been to apply standard techniques to seven solutes in this solvent, and to compare results so secured with others already known from work with carbon tetrachloride, benzene. hexane, etc. The present paper logically follows that by Armstrong *et al.*,[2] which dealt with binary mixtures of non-polar components. Cases of polar solutes in non-polar solvents have previously been discussed by Le Fèvre and Le Fèvre [3] and by Buckingham.[4]

[1] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.
[2] Armstrong, Aroney, Le Fèvre, Le Fèvre, and Smith, *J.*, 1958, 1474.
[3] Le Fèvre and Le Fèvre, *J.*, 1953, 4041; 1954, 1577; 1955, 2750.
[4] Buckingham, *Trans. Faraday Soc.*, 1956, **52**, 611.

Experimental

Materials, Apparatus, etc.—Solutes were dried and redistilled or recrystallised, as appropriate, immediately before their solutions were prepared. Bulk supplies of chloroform were at first treated as specified by Vogel.[5] Later, when the low electric birefringence of ethanol (commonly present in commercial chloroform) became known,[6] we found that 24 hours over calcium chloride followed by fractionation through a 1 m. column packed with glass helices produced a solvent satisfactory for present purposes. Apparatus already described [1,3,7,8] for measurements of Kerr effects and dielectric constants has been used without change except for minor alterations due to the electrical and optical properties of chloroform. Observations are listed in Table 1 under the headings: w_2, weight fractions; ε, dielectric constants; d, densities; and ΔB and Δn_D, increments in the Kerr constant and refractive index (Na light) from solvent to solutions. Subsequent calculations of apparent polarisations, moments, and molar Kerr constants at infinite dilution are given in Tables 2 and 3. Appropriate data for chloroform as a solvent at 25° and with $\lambda = 5893$ Å are: $\varepsilon = 4{\cdot}724$, $H = 2{\cdot}040$, ${}_sK_1 = -0{\cdot}1474 \times 10^{-12}$, $d = 1{\cdot}4790$, $J = 0{\cdot}2974$, $p_1 = 0{\cdot}37447$, $n_D = 1{\cdot}4430$, $B = -3{\cdot}22 \times 10^{-7}$, $C = 0{\cdot}04486$. These, and other symbols used later, are explained in ref. 1, p. 283, and ref. 8, p. 56.

Discussion

Observed Molar Kerr Constants.—In all cases except that of naphthalene the values of apparent ${}_\infty({}_mK_2)$ of Table 3 are algebraically lower than those obtained before [1,2,9] with carbon tetrachloride as solvent:

Solute	C_6H_6	C_6H_5Cl	$C_6H_5{\cdot}NO_2$	$C_{10}H_8$	$C_{14}H_{10}$	CS_2	CCl_4
${}_\infty({}_mK_2)_{CCl_4} \times 10^{12}$	7·2	145	1073	48·1	82·6	27·8	1·1
Reference	1	1	1	1	9	2	1
${}_\infty({}_mK_2)_{CHCl_3} \times 10^{12}$ ...	−5·2	101·5	744	51·4	71·0	17·0	−7·1

In ref. 2 it was demonstrated that a molecular polarisability semi-axis, as measured by experiment, appears to be influenced by the refractive index of the medium and by a " shape factor " k_i for the solute concerned; equations of the type

$$b_i^{\text{soln}}/b_i^{\text{vapour}} = 1 - K(n_1^2 - 1)(0{\cdot}333 - k_i)/(n_1^2 + 2)$$

(in which K could be 1, n_1, or n_1^2) were shown to represent this phenomenon adequately enough to forecast the variations of the molar Kerr constants of non-polar substances from solvent to solvent. Accordingly, since the refractive indexes of carbon tetrachloride and chloroform are about the same (1·4575 and 1·4430 respectively at 25°), so should be the semi-axes of a molecule dissolved in each of these liquids, provided the structure (shape) is similar in the two environments. As an initial step, therefore, we assume that the anisotropy term θ_1 (see ref. 1, p. 270, for definition) for a given solute in carbon tetrachloride is an acceptable approximation for the θ_1 of that solute when in chloroform.

The anisotropy terms for chloro- and nitro-benzene in carbon tetrachloride have been reported by Le Fèvre and Rao [10] as $4{\cdot}29 \times 10^{-35}$ and $5{\cdot}57 \times 10^{-35}$; from the present paper, and other details in ref. 10, it follows that the " dipole terms " θ_2 in the two media are in the ratios, for chlorobenzene $19{\cdot}9/30{\cdot}2 = 0{\cdot}66$, and for nitrobenzene, $171/250 = 0{\cdot}68$. According to Le Fèvre and Le Fèvre,[3] these ratios should resemble those for $\mu^2_{CHCl_3}/\mu^2_{CCl_4}$, which are 0·59 with chlorobenzene and 0·62 with nitrobenzene. Agreement is reasonable, in view of the nature of the measurements involved, and in accordance with the idea that apparent moments are much more strongly affected by the medium than are polarisability semi-axes.

[5] Vogel, " Practical Organic Chemistry," Longmans, Green & Co., London, 3rd edn., 1956, p. 176.
[6] Le Fèvre, Le Fèvre, Rao, and Williams, *J.*, 1960, 123.
[7] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.
[8] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, p. 45.
[9] Le Fèvre and Le Fèvre, unpublished.
[10] Le Fèvre and Rao, *J.*, 1958, 1465.

TABLE 1. *Kerr constants, refractivities, dielectric constants, and densities of solutions in chloroform containing weight fractions* w_2 *of solute at 25°.*

Solute: *Benzene*

10^5w_2	1468	3612	5647	5990	7108	7418	10,221	11,282	
d_4^{25}	1·4641	1·4429	1·4234	1·4200	1·4095	1·4067	1·3814	1·3718	
$10^4\Delta n_D$ ...	13	30	47	49	58	60	81	89	
10^5w_2	4064	4362	5445	5794	6555	6852	8640	9708	9757
ε^{25}	4·494	4·478	4·421	4·407	4·363	4·349	4·262	4·217	4·219
10^5w_2	11,251	12,296	15,151						
ε^{25}	4·147	4·105	3·991						

whence $\Delta\varepsilon = -5{\cdot}95w_2 + 7{\cdot}41w_2^2$; $\Delta d = -1{\cdot}023w_2 + 0{\cdot}65w_2^2$

10^5w_2	2948	3004	3051	4076	4581	4636	4774	4828	6154
$10^7\Delta B$ ...	0·218	0·197	0·328	0·404	0·425	0·430	0·403	0·393	0·527
$10^4\Delta n_D$ ...	—	—	24	34	—	—	—	—	—
10^5w_2	6267	6836	7741	8513	9125	9839	9884	13,545	21,030
$10^7\Delta B$ ...	0·567	0·654	0·665	0·735	0·780	0·835	0·767	—	—
$10^4\Delta n_D$ ...	52	—	62	—	—	—	—	105	160

whence $\sum(\Delta B\,.\,w_2)/\sum w_2^2 = +8{\cdot}59$; or $\sum\Delta B/\sum w_2 = +8{\cdot}65$; or $10^7\Delta B = +9{\cdot}511w_2 - 11{\cdot}98w_2^2$; and $\sum\Delta n/\sum w_2 = 0{\cdot}0796$.

Solute: *Chlorobenzene*

10^5w_2	5299	5546	5950	6402	6578	7042	7062	7574
d_4^{25}	1·4530	1·4521	1·4502	1·4478	1·4472	1·4444	1·4447	1·4424
10^5w_2	8997	9427	12,031	12,714	12,984	13,725		
d_4^{25}	1·4360	1·4338	1·4218	1·4183	1·4177	1·4140		

whence $\sum\Delta d/\sum w_2 = -0{\cdot}4811$

10^5w_2	5403	5781	8159	8170	9386	11,625	12,525	17,128
ε^{25}	4·791	4·795	4·821	4·821	4·836	4·863	4·876	4·926

whence $\sum\Delta\varepsilon/\sum w_2 = 1{\cdot}19_9$

10^5w_2	2151	2803	3229	3792	5302	5728	6068	6127	7176	8420	11,206
$10_4\Delta n_D$ ...	33	40	45	52	65	71	74	75	86	100	130

whence $\sum\Delta n/\sum w_2 = 0{\cdot}1244$

10^5w_2	2113	3377	3863	5403	5781	6328	8170	9386
$10^7\Delta B$ ...	0·51	0·74	0·85	1·21	1·27	1·42	1·87	2·12

whence $\sum\Delta B/\sum w_2 = 22{\cdot}49$

Solute: *Nitrobenzene*

10^5w_2	682	1227	1388	1943	2021	2415	2597	2904
d_4^{25}	1·4770	1·4752	1·4746	1·4732	1·4729	—	1·4713	1·4703
$10^4\Delta n_D$ ...	10	15	18	23	24	35	33	37
10^5w_2	3483	4443	8126	9566	14,696			
d_4^{25}	1·4686	1·4657	1·4573	1·4534	1·4390			
$10^4\Delta n_D$ ...	56	58	113	134	200			

whence $\Delta d = -0{\cdot}291w_2 + 0{\cdot}15w_2^2$; $\sum\Delta n/\sum w_2 = 0{\cdot}1363$

10^5w_2	1038	1523	2264	2283	2412	2919
ε^{25}	5·054	5·208	5·441	5·445	5·486	5·645

whence $\sum\Delta\varepsilon/\sum w_2 = 31{\cdot}6_3$

10^5w_2	261	290	412	539	548	594	663	697	794	872	892	1005	1175	1226
$10^7\Delta B$ ...	0·23	0·22	0·45	0·61	0·64	0·64	0·70	0·73	0·87	0·99	0·98	1·01	1·16	1·27

whence $\sum\Delta B/\sum w_2 = 105{\cdot}3$

Solute: *Naphthalene*

10^5w_2	1694	1776	2357	2953	3977	4009	6436	
d_4^{25}	1·4684	1·4679	1·4644	1·4607	1·4546	1·4544	1·4397	
10^5w_2	1612	2103	2935	3347	3426	4244	5151	5213
ε^{25}	4·654	4·632	4·596	4·578	4·576	4·540	4·504	4·501

whence $\sum\Delta\varepsilon/\sum w_2 = -4{\cdot}30_6$; $\sum\Delta d/\sum w_2 = -0{\cdot}6199$

10^5w_2	928	1143	1736	1769	2572	2754	2789	3315
$10^7\Delta B$ ...	0·131	0·209	0·319	0·316	0·436	0·472	0·510	0·525
$10^4\Delta n_D$ ...	22	29	45	46	68	71	70	88
10^5w_2	3506	3978	4053	5099	5532	6319	7952	
$10^7\Delta B$ ...	0·591	0·663	0·667	0·754	0·831	0·919	0·984	
$10^4\Delta n_D$ ...	91	103	106	132	139	161	170	

whence $\sum\Delta B/\sum w_2 = +16{\cdot}9_5$; or $\sum\Delta B\,.\,w_2/\sum w_2^2 = +16{\cdot}86$; and $\sum\Delta n/\sum w_2 = 0{\cdot}2508$

TABLE 1. (*Continued.*)

Solute: *Phenanthrene*

10^5w_2	548	1095	1434	1738	1789	1835	2136	2325	2392	2397	2648
d_4^{25}	1·4768	—	1·4729	1·4714	1·4714	1·4708	1·4699	—	1·4685	1·4687	1·4676
$10^4\Delta n_D$ ...	16	37	—	60	64	62	78	82	88	86	95
10^5w_2	3158	3270	3403	3578	3794	3996	4036	4784	4895	5437	5868
d_4^{25}	1·4649	1·4649	1·4641	1·4637	1·4623	1·4615	—	1·4581	1·4575	1·4553	1·4535
$10^4\Delta n_D$ ...	110	—	119	125	—	141	142	163	—	187	202
10^5w_2	2634	2845	4106	4954	5771	6220					
ε^{25}	4·633	4·626	4·583	4·552	4·524	4·514					

whence $\sum\Delta\varepsilon/\sum w_2 = -3{\cdot}44$; $\sum\Delta d/\sum w_2 = -0{\cdot}4365$; $\sum\Delta n/\sum w_2 = 0{\cdot}2418$

10^5w_2	1020	1039	1428	1517	2464	2661	3505	3632	4349	5383
$10^7\Delta B$ ...	0·15	0·18	0·23	0·24	0·38	0·41	0·52	0·55	0·69	0·81

whence $\sum\Delta B/\sum w_2 = 15{\cdot}41$; or $\sum\Delta B\,.\,w_2/\sum w_2^2 = 15{\cdot}32$

Solute: *Carbon disulphide*

10^5w_2	3830	4140	7526	8444	9397	12,694
d_4^{25}	1·4675	1·4665	1·4567	1·4542	1·4513	1·4423
$10^4\Delta n_D$ ...	71	75	137	151	169	230
10^5w_2	2816	4375	4507	5721	8279	8567
ε^{25}	4·632	4·581	4·578	4·540	4·463	4·456

whence $\sum\Delta\varepsilon/\sum w_2 = -3{\cdot}19_3$; $\Delta d = -0{\cdot}306w_2 + 0{\cdot}14w_2^2$

10^5w_2	927	1382	2226	2326	2657	3240	3319
$10^7\Delta B$ ...	—	0·238	0·261	0·291	—	0·400	0·378
$10^4\Delta n_D$ ...	18	24	39	41	50	58	59
10^5w_2	3737	4946	5835	6533	7419	7651	9349
$10^7\Delta B$ ...	0·444	0·565	0·645	0·750	0·859	0·828	1·062
$10^4\Delta n_D$ ...	68	88	105	119	132	130	165

whence $\sum\Delta B/\sum w_2 = 11{\cdot}60$; or $\sum\Delta B\,.\,w_2/\sum w_2^2 = 11{\cdot}40$; and $\sum\Delta n/\sum w_2 = 0{\cdot}1793$

Solute: *Carbon tetrachloride*

10^5w_2	2508	2570	2738	3520	3555	3838	4249	5312	6543	6573
d_4^{25}	—	—	1·4818	—	—	1·4828	—	—	1·4854	—
$10^4\Delta n_D$ ...	4	3	3	4	4	4	6	6	7	7
10^5w_2	6644	7612	8479	8842	9537	10,089	13,366	14,891	16,456	
d_4^{25}	—	—	1·4873	—	1·4884	—	1·4921	—	—	
$10^4\Delta n_D$ ...	7	8	10	10	11	14	15	19	21	
10^5w_2	3176	5188	6370	8509	8717	11,294	14,786			
ε^{25}	4·631	4·575	4·539	4·482	4·474	4·406	4·308			

whence $\sum\Delta\varepsilon/\sum w_2 = -2{\cdot}85$; $\sum\Delta d/\sum w_2 = +0{\cdot}0984$; and $\sum\Delta n/\sum w_2 = 0{\cdot}0112$

10^5w_2	3094	4477	5434	5999	7213	7906	8568	9708	12,227	12,776
$10^7\Delta B$ ...	0·12	0·19	0·25	0·30	0·34	0·39	0·43	0·48	0·60	0·60
10^5w_2	14,745	15,873	17,427							
$10^7\Delta B$ ...	0·68	0·71	0·81							

whence $\sum\Delta B/\sum w_2 = -4{\cdot}70$; or $\sum\Delta B\,.\,w_2/\sum w_2^2 = -4{\cdot}69$

TABLE 2. *Total polarisations at infinite dilution, and apparent dipole moments, calculated from Table* 1.

Solute	$(\alpha\varepsilon_1)_{w_2=0}$	$(\beta)_{w_2=0}$	${}_\infty P_2$ (c.c.)	R_D (c.c.)	$\mu_{app.}$ (D)
Benzene	−5·95	−0·692	28·6$_3$	25·9	0·3$_6$
Chlorobenzene	1·20	−0·325	61·9	31·7	1·2$_2$
Nitrobenzene	31·6	−0·197	229·8	32·4	3·1$_1$
Naphthalene	−4·31	−0·419	43·3$_5$	44·3	*ca.* 0
Phenanthrene	−3·44	−0·295	58·9$_4$	63·5	*ca.* 0
Carbon disulphide	−3·19	−0·207	23·5$_1$	21·3	0·3$_2$
Carbon tetrachloride	−2·85	0·067	34·1$_2$	26·6	0·6$_1$

TABLE 3. *Molar Kerr constants and sums of anisotropy and dipole terms at infinite dilution calculated from Tables* 1 *and* 2.

Solute	γ	δ	${}_\infty({}_mK_2) \times 10^{12}$	$(\theta_1 + \theta_2) \times 10^{35}$
Benzene	0·055	−2·95	−5·2$_4$	−1·2$_5$
Chlorobenzene	0·086	−6·98	101·5	24·1$_4$
Nitrobenzene	0·094	−32·7	743·9	176·9
Naphthalene	0·173	−5·24	51·4	12·2
Phenanthrene........................	0·241	−4·77	71·0	16·9
Carbon disulphide	0·124	−3·54	17·0	4·0$_4$
Carbon tetrachloride	0·008	−1·46	−7·0$_8$	−1·6$_8$

Turning now to the five normally non-polar solutes in Tables 2 and 3, we must conclude that in chloroform they exhibit θ_2 terms:

Solute	C_6H_6	$C_{10}H_8$	$C_{14}H_{10}$	CS_2	CCl_4
Apparent $\theta_2 \times 10^{35}$	$-3{\cdot}0$	$+0{\cdot}8$	$-2{\cdot}7$	$-2{\cdot}6$	$-1{\cdot}7$

Such features point to the possession by these species of finite dipole moments, and are of interest in relation to previous [11-13] observations which had also suggested that non-polar solutes might become polar in polar media. The negative signs now noted for these values of θ_2 indicate that the apparent moments are developed in directions roughly perpendicular to the greatest polarisability axis of the dissolved particle, whatever this is—it might be some sort of loose adduct of chloroform with either a distorted or an undistorted form of the non-polar solute. On the probably over-simple assumption that benzene and carbon disulphide (semi-axes $\times 10^{23}$: 1·12, 1·12, $0{\cdot}73_5$ and 1·308, 0·558, 0·558 respectively [2]) are undistorted and behave independently of the chloroform molecules, dipole moments of 0·3—0·4 D would, if acting parallel to the b_3 directions, produce *negative* θ_2's about one-third to one-half of those found. With carbon tetrachloride (for which θ_1 is zero [14]) some distortion must be presumed. If μ_{C-Cl} is taken as *ca.* 1·6 D, then an apparent moment for carbon tetrachloride of 0·6 D implies modification of the tetrahedral model so that three of the Cl–C–Cl angles become 102°; with the values $b_L^{C-Cl} = 0{\cdot}399 \times 10^{-23}$ and $b_T^{C-Cl} = 0{\cdot}185 \times 10^{-23}$, the semi-axes for the distorted molecule would be $0{\cdot}982 \times 10^{-23}$ (along the line of action of $\mu_{resultant}$) and $1{\cdot}049 \times 10^{-23}$ (in the two directions perpendicular to $\mu_{resultant}$). These are to be compared with $b_1 = b_2 = b_3 = 1{\cdot}02_6 \times 10^{-23}$ ordinarily determined. The difference, $b_1 — b_2 = -0{\cdot}067 \times 10^{-23}$, combined with a moment of 0·6 D, leads to a θ_2 term of $-0{\cdot}63 \times 10^{-35}$, namely, about one-third of that actually recorded. It seems therefore that either the negativity of our θ_2 values has been overestimated or the apparent moments deduced are too small. The use of chloroform as a solvent in the measurement both of electric double refraction and of dielectric polarisation involves practical difficulties which are not present with the usual non-polar media, although, even in these, moments estimated from orientation polarisations of a few c.c. are notoriously uncertain (ref. 8, p. 25). We suspect the values of $\mu_{apparent}$ more than those of θ_2; to accept the former as real and to attempt the extraction of polarisability semi-axes in the usual way is dangerous because $45k^2T^2\theta_2/\mu^2_{apparent}$ is sensitively affected by $\mu^2_{apparent}$, small errors in which are much magnified in the quotient, *i.e.*, in the quantity $2b_1 - b_2 - b_3$.

With chloro- and nitro-benzene, however, the situation is better: using the apparent moments and θ_2's in Tables 2 and 3, we find semi-axes which are close to those previously noted [10] in carbon tetrachloride:

	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
C_6H_5Cl in $CHCl_3$	1·53	1·21	0·84
C_6H_5Cl in CCl_4	1·48	1·26	0·82
$C_6H_5{\cdot}NO_2$ in $CHCl_3$	1·67	1·06	0·93
$C_6H_5{\cdot}NO_2$ in CCl_4	1·62	1·20	0·86

Apparent Moments of Chloro- and Nitro-benzene in Chloroform.—Values (in D) have been previously reported as: $\mu_{PhCl} = 1{\cdot}18$; [12] $\mu_{PhNO_2} = 3{\cdot}30$,[15] 3·24,[16] 3·17,[17] 3·05,[12] 3.15.[18] Although the μ's ($1{\cdot}2_2$ and $3{\cdot}1_1$ D) given in Table 2 for chloro- and nitro-benzene are reconcilable with most of these earlier data, it is nevertheless our experience that the determination of $\mu_{apparent}$ in chloroform is a less reliable procedure generally than when benzene, carbon tetrachloride, etc., are taken as solvents: the cases of naphthalene and

11 Le Fèvre and Le Fèvre, *J.*, 1936, 487.
12 Le Fèvre and Russell, *J.*, 1936, 491.
13 Holland and Le Fèvre, *J.*, 1950, 2166.
14 Le Fèvre, Le Fèvre, and Rao, *J.*, 1956, 708; Le Fèvre and Le Fèvre, *J.*, 1959, 2670.
15 Hassel and Uhl, *Z. phys. Chem.*, 1930, *B*, **8**, 199.
16 Hassel and Naeshagen, *Naturwiss.*, 1930, **18**, 24.
17 Jenkins, *Nature*, 1934, **133**, 106; *J.*, 1934, 482.
18 Smith and Cleverdon, *Trans. Faraday Soc.*, 1949, **45**, 109.

phenanthrene, where R_D's calculated from the observed n_{12}'s and d_{12}'s inexplicably exceed the $_\infty P_2$'s, illustrate one of the uncertainties. This has relevance to the point of the last paragraph. If, *e.g.*, with nitrobenzene, a small change be imagined in $\mu_{apparent}$, recomputation will reveal that a notable alteration follows of the principal polarisabilities, especially of b_2 and b_3:

μ (D)	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
$3{\cdot}1_1$	1·67	1·06	0·93
$3{\cdot}2_1$	1·64	1·16	0·86
$3{\cdot}3_1$	1·62	1·22	0·83

Conclusion.—These results suggest that chloroform can be used as solvent for this work only with strongly polar solutes whose apparent moments in chloroform can be measured accurately.

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