545. *Molecular Polarisability. The Molar Kerr Constants of Benzyl Alcohol and Aniline at Infinite Dilution.*

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The molar Kerr constants of benzyl alcohol in carbon tetrachloride or benzene, and of aniline, dimethylaniline, and diethylaniline in benzene are found to be *positive* at infinite dilution. The first two solutes show *negative* ${}_{\mathrm{m}}K$'s as pure liquids. Suggestions made earlier, based upon dielectric polarisation observations, are thus verified by experiment. Aniline must have a pyramidal configuration; it cannot be the flat Y forecast by considerations of resonance. The polymers of benzyl alcohol or aniline, formed by hydrogen bonding in concentrated solutions, exhibit negative electric double refraction. The dialkylanilines, in which hydrogen bonding is impossible, exhibit positive Kerr effects both as pure liquids and at infinite dilution.

It has recently been demonstrated [1] that the "true" dipole moment of benzyl alcohol (determined as a gas) is greater than the apparent value deduced from measurements on solutions in benzene. Previous work [2] had indicated that aniline behaved similarly. The interest of these cases lay in the fact that the two solutes in bulk have *negative* Kerr constants [3] and, on earlier ideas,[4–10] should therefore have been expected to exhibit $\mu_{\text{soln.}}/\mu_{\text{gas}}$ ratios of more than unity. Le Fèvre, Roberts, and Smythe [2] suggested that aniline would not be anomalous if the algebraic sign of the Kerr constant appropriate for separate molecules (*i.e.*, the constant at infinite dilution) were *positive.*

The present paper records (*a*) dielectric-polarisation data for the system benzyl alcohol–carbon tetrachloride, and (*b*) electric double-refraction observations on benzyl alcohol, aniline, dimethylaniline, and diethylaniline, dissolved in benzene, and on benzyl alcohol dissolved in carbon tetrachloride.

From (*a*) we find for benzyl alcohol at 25°: $({}_{\infty}P_2)_{\mathrm{CCl_4}} = 93{\cdot}9$ c.c., $R_{\mathrm{D}} = 32{\cdot}5$ c.c., whence $\mu_{\text{apparent}} = 1{\cdot}72$ D. For benzyl alcohol therefore the $\mu_{\text{soln.}}/\mu_{\text{gas}}$ quotient is *ca.* 1 (Buckingham, Holland, and Le Fèvre [1] reported μ_{gas} as 1·71 D, but their polarisations were computed relatively to benzene the polarisation of which was taken as 26·62 c.c. Since we now believe $P_{\text{benzene (gas)}}$ to be at least 27·0 c.c.—cf. Le Fèvre and Rao [11]—the value 1·71 D requires raising slightly.

From (*b*) we find that ΔB (the difference between B_{12} and B_1) depends on concentration as follows:

System	w_2 range, 0 to	$10^7\Delta B$
Benzyl alcohol–CCl_4	0·062	$3{\cdot}44w_2 - 71{\cdot}1w_2^2 + 237w_2^3$
Benzyl alcohol–benzene	0·090	$2{\cdot}16w_2 - 61{\cdot}7w_2^2 + 360w_2^3$
Aniline–benzene	0·298	$1{\cdot}50w_2 - 8{\cdot}02w_2^2 + 12{\cdot}2w_2^3$
Dimethylaniline–benzene	0·03	$6{\cdot}13w_2 + 41w_2^2$
Diethylaniline–benzene	0·02	$7{\cdot}03w_2 + 81w_2^2$

(The symbols used throughout are those defined [12, 13] by Le Fèvre and Le Fèvre.) Investigation of the last two cases was not extended to higher values of w_2 since the pure dialkylanilines have positive Kerr constants and no inflexion of the ΔB–w_2 curve was to be expected. Leiser [3] quotes electric birefringences, relatively to that of carbon disulphide,

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[1] Buckingham, Holland, and Le Fèvre, *J.*, 1954, 1646.

[2] Le Fèvre, Roberts, and Smythe, *J.*, 1949, 902.

[3] Leiser, "Abhandlungen der deutschen Bunsen-Gesellschaft," 1910, Nr. 4.

[4] Le Fèvre and Le Fèvre, *J.*, 1935, 1747.

[5] Le Fèvre, *Nature*, 1935, **136**, 181.

[6] Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374.

[7] Le Fèvre and Ross, *J.*, 1950, 283.

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[10] Angyal, Barclay, and Le Fèvre, *J.*, 1950, 3370.

[11] Le Fèvre and Rao, *Austral. J. Chem.*, 1955, **8**, 39.

[12] Le Fèvre and Le Fèvre, *J.*, 1953, 4041.

[13] *Idem*, *J.*, 1954, 1577.

as $C_6H_5{\cdot}CH_2{\cdot}OH$, −4·77; aniline, −0·38; dimethylaniline, +3·12; and diethylaniline, +3·23; Lippmann[14] gives aniline as −0·507. Application of the absolute values of B_{CS_2} cited by the I.C.T.[15] therefore produces, for $w_2 = 1$, 10^7B_2 as:

$$B_{C_6H_5\cdot CH_2\cdot OH} = -15{\cdot}4 \qquad B_{C_6H_5\cdot NMe_2} = +10{\cdot}1$$

$$B_{C_6H_5\cdot NH_2} = -1{\cdot}23 \text{ or } -1{\cdot}64 \qquad B_{C_6H_5\cdot NEt_2} = +10{\cdot}4$$

Our first three equations (above) require maxima for ΔB at $w_2 = 0{\cdot}028$, 0·032, and 0·109, respectively. Figs. 1 and 2 show certain of the present results graphically; Fig. 1 includes the points from Lippmann[14] to which reference was made by Le Fèvre, Roberts, and Smythe.[2]

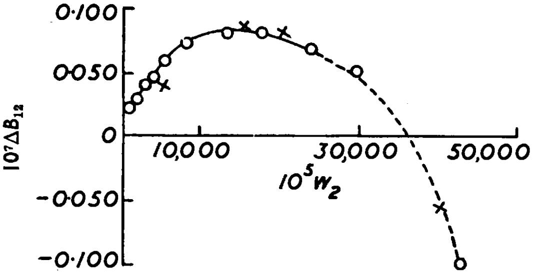

FIG. 1. Aniline.

× = Points due to Lippmann.[14]

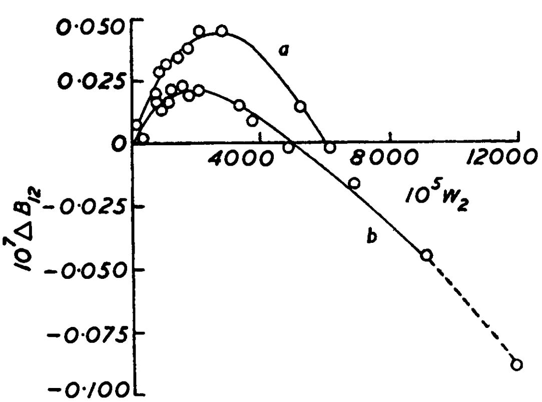

FIG. 2.

(*a*) Benzyl alcohol–carbon tetrachloride.
(*b*) Benzyl alcohol–benzene.

EXPERIMENTAL

The apparatus, techniques, and methods of calculation employed have been those of Le Fèvre and Le Fèvre.[12, 13] The solutes were purified by distillation immediately before use. Observations are given in Tables 1—3.

TABLE 1. *Dielectric constants and densities of benzyl alcohol in carbon tetrachloride at 25°.*

10^5w_2 ...	0	627	727	848	1135	1343	1613	1697	2210	2565	2974
ε_{25}	2·2270	2·2628	2·2686	2·2729	2·2888	2·3003	2·3131	2·3152	2·3428	2·3642	2·3821
d_4^{25}	1·5845	1·5792	1·5784	1·5773	1·5752	1·5733	1·5711	1·5706	1·5663	1·5630	1·5605

whence $\Delta\varepsilon = (5{\cdot}55 \pm 0{\cdot}07)w_2 - 11{\cdot}76w_2^2$; $\Delta d = (-0{\cdot}848 \pm 0{\cdot}020)w_2 + 1{\cdot}08w_2^2$

TABLE 2. *Electric double refractions in carbon tetrachloride at 25°.*

Benzyl alcohol

10^5w_2	186	753	765	868	925	1031	1391
$10^7\Delta B$	0·008	0·019	0·020	0·029	0·031	0·032	0·036
Δn_D	0·000	0·0006	—	—	—	0·0011	—
10^5w_2	1669	2088	2805	5261	6181	15,536	
$10^7\Delta B$	0·038	0·047	0·046	0·015	−0·002	−0·300	
Δn_D	0·0017	—	0·0034	0·0068	—	—	

Molar Kerr Constants at Infinite Dilution.—Values of $_\infty(_mK_2)$ have been calculated by the methods given in refs. 12 and 13. In the estimation of $\partial(\Delta B)/\partial w_2$ as w_2 approaches zero we

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[14] Lippmann, Diss., Leipzig, 1911.

have avoided ΔB's which are near or over the maxima of the ΔB–w_2 relations. Thus by least squares we obtain for

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\begin{array}{llll}
C_6H_5{\cdot}NH_2\text{–}C_6H_6, & \text{using } w_2\text{'s up to } 0{\cdot}131, & 10^7\Delta B & = 1{\cdot}55w_2 - 7{\cdot}10w_2^2 \\
C_6H_5{\cdot}CH_2{\cdot}OH\text{–}C_6H_6, & \text{,, ,, ,, ,, } 0{\cdot}016, & \text{,,} & = 2{\cdot}20w_2 - 34{\cdot}2w_2^2 \\
C_6H_5{\cdot}CH_2{\cdot}OH\text{–}CCl_4, & \text{,, ,, ,, ,, } 0{\cdot}028, & \text{,,} & = 3{\cdot}34w_2 - 59{\cdot}6w_2^2
\end{array}
$$

It will be noted that the coefficients of w_2 are not seriously affected by the use of either a two-term or a three-term power equation in w_2. The continuous curves in Figs. 1 and 2 correspond to the three-term relations already quoted; they have not been pursued further than the limits mentioned since inclusion of larger w_2's makes imperative the introduction of negative fourth terms, containing w_2^4, whose computation is tedious and unnecessary for present purposes. Table 4 contains the data from which are deduced the molar Kerr constants at infinite dilution.

TABLE 3. *Electric double refractions in benzene at* 25°.

Aniline

10^5w_2 ...	1044	1905	2871	3936	5581	7606	13,102	17,548	24,107	29,819	42,580
$10^7\Delta B$...	0·023	0·031	0·042	0·048	0·061	0·075	0·082	0·083	0·071	0·054	–0·098
Δn	0·0009	0·0016	—	0·0031	0·0044	0·0062	0·0109	0·0144	0·0201	0·0241	0·0348

Dimethylaniline

10^5w_2 ...	344	664	1220	1514	2242	2670
$10^7\Delta B$...	0·014	0·044	0·074	0·110	0·163	0·190
Δn	0·0003	0·0009	0·0011	0·0015	0·0015	—

Diethylaniline

10^5w_2 ...	324	642	1043	1399	1769	2195
$10^7\Delta B$...	0·012	0·043	0·082	0·124	0·152	0·189
Δn	0·0001	0·0004	0·0005	0·0007	0·0007	—

Benzyl alcohol

10^5w_2 ...	337	687	730	848	948	1076	1157	1217	1606
$10^7\Delta B$...	0·002	0·014	0·016	0·013	0·016	0·023	0·022	0·025	0·024
Δn	—	0·0002	—	—	—	—	—	—	—
10^5w_2 ...	1792	2016	3280	3572	4749	7005	8980	11,808	
$10^7\Delta B$...	0·019	0·020	0·014	0·007	–0·003	–0·016	–0·046	–0·088	
Δn	0·0008	—	0·0011	—	0·0018	0·0028	0·0034	0·0042	

TABLE 4. *Molar Kerr constants at infinite dilution.*

Solute	Solvent	$\alpha\varepsilon_1$	β	γ	δ	$_\infty(_mK_2) \times 10^{12}$
$C_6H_5{\cdot}CH_2{\cdot}OH$	CCl_4	5·55	–0·535	0·080	47·7	37·7
,,	C_6H_6	2·90 *	0·162$_5$ *	0·025	5·36$_5$	39·4
$C_6H_5{\cdot}NH_2$	,,	2·95 †	0·153$_4$ †	0·055	3·78	22·4
$C_6H_5{\cdot}NMe_2$	,,	2·47 ‡	0·082$_4$ ‡	0·059	14·9$_5$	134·2
$C_6H_5{\cdot}NEt_2$	,,	2·48$_5$	0·058$_4$	0·031	17·1$_5$	190·6

* From ref. 1. † From ref. 2. ‡ From ref. 16.

DISCUSSION

It is evident that, in their unimolecular states, both benzyl alcohol and aniline have *positive* Kerr constants, and accordingly, that the $\mu_{\text{soln.}}/\mu_{\text{gas}}$ ratios for these substances conform qualitatively to the qualitative generalisation of Le Fèvre and Le Fèvre.[4] Doubt is thus thrown on discussions by a number of authors [17, 18] who have attempted to harmonise dielectric data with a *negative* Kerr constant for aniline. Present results therefore support the suggestions made in refs. 1 and 2, *viz.*, that negativity of the Kerr constants of benzyl alcohol and aniline is a property of the liquid substances only, and arises from the presence of association complexes or cybotactic aggregates whose anisotropic polarisabilities are not the same as those of the separated molecules, with which one is dealing at infinite dilution.

[15] International Critical Tables, Vol. VII.

[16] Barclay, Le Fèvre, and Smythe, *Trans. Faraday Soc.*, 1951, **47**, 357.

[17] Higasi, *Bull. Inst. Chem. Phys. Res. Tokyo*, 1934, **13**, 1167.

[18] Cowley and Partington, *J.*, 1938, 1598.

Le Fèvre *et al.*[2] have already remarked that association of aniline by hydrogen bonding could produce a dimer having some stereo-resemblance to hydrazobenzene (the N–H–N unit being rectilinear), the Kerr effect of which is *negative.*[14] Consistently with this, when hydrogen bonding is prevented by alkylation (as in dimethyl- and diethyl-aniline), not only is $_{\infty}({}_{\mathrm{m}}K_2)$ positive but the positivity—unlike that with aniline—is retained through increasing concentrations up to the pure solutes, which also display positive ${}_{\mathrm{m}}K$'s.

Correlations between present results and studies of association based on infrared spectra [19-23] are difficult to make because quantitative absorption data are sparse.

The *positive* value of $_{\infty}({}_{\mathrm{m}}K_2)$ now obtained for aniline has implications regarding the configuration of this base. Rao [24] has recorded a depolarisation factor of 0·061, whence $\delta_0{}^2 = 0{\cdot}109_5$ (cf. equation 3 of ref. 13). Vogel [25] gives R_{C}, R_{D}, and R_{F} from which $R_{\infty} = {}_{\mathrm{E}}P$ follows as 29·1 c.c. The sum of the semi-axes of the aniline polarisability ellipsoid is therefore

$$b_1 + b_2 + b_3 = 3{\cdot}440 \times 10^{-23}$$

and

$$(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2 = 1{\cdot}295_5 \times 10^{-46}$$

Accordingly θ_1 is $7{\cdot}70 \times 10^{-35}$. The total $(\theta_1 + \theta_2)$ is $5{\cdot}33 \times 10^{-35}$ (from the molar Kerr constant in Table 4) so that θ_2 is $-2{\cdot}37 \times 10^{-35}$. If the resultant moment μ of aniline acts in the plane containing the axes b_1 and b_2 and at an angle β with the former, then

$$45k^2T^2\theta_2 = \mu^2[3\cos^2\beta(b_1 - b_2) + 2b_2 - b_1 - b_3]$$

and four unknowns (b_1, b_2, b_3, and β) are involved. Since from experiment only three equations are available the case cannot be analysed quantitatively. Nevertheless it is clear that aniline is not the flat Y-shaped molecule forecast by considerations of resonance (but cf. refs. 26, 27) because were it so $\mu_{\mathrm{resultant}}$ would lie along b_{maximum} making θ_2 positive. Maccoll (quoted by Ingold [28]) has noted " that it is an assumption, still in need of experimental confirmation, that the aniline molecule is accurately flat . . . " The value of $_{\infty}({}_{\mathrm{m}}K_2)$ of this amine strengthens the suspicion thus implied and strongly suggests that a pyramidal structure for aniline is correct. Relaxation data, reviewed by Davies,[29] are in accord with the last remark. From dipole-moment measurements alone, Marsden and Sutton [30] had concluded in 1936 that $\mu_{\mathrm{resultant}}$ in aniline is at 43—44° to the C–N bond.

Finally, we mention an obvious fact : that aniline and benzyl alcohol, having negative values of ${}_{\mathrm{m}}K_{\mathrm{liquid}}$, are exceptions to the empirical rule of Le Fèvre and Le Fèvre [12] whereby ${}_{\mathrm{m}}K_{\mathrm{liq.}}$ multiplied by ε/n^2 becomes roughly $_{\infty}({}_{\mathrm{m}}K_2)$.

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