445. *The Apparent Induction of Polarity in Non-polar Solutes by Polar Solvents.*

By H. G. Holland and R. J. W. Le Fèvre.

Earlier observations of the phenomena covered by the title have been repeated and extended, and a more certain extrapolation procedure applied. Solutes such as carbon disulphide, benzene, *cyclo*hexane, diphenyl, etc., dissolved in nitrobenzene appear to develop moments ranging from 1·2 to 2 D. The effects are not smoothly proportional to the corresponding molecular refractions, but use of the latter in conjunction with dimensions read off scale drawings has afforded an empirical equation, $\mu^2_{\text{induced}} = \mu^2_2 . R_1\text{Exp.}(-h^2)/A_2B_2C_2$, by which the experimental results in chloro- as well as nitro-benzene may be satisfactorily forecast.

Le Fèvre and Le Fèvre (*J.*, 1936, 487), from measurements of the dielectric constants and densities of dilute solutions of benzene, carbon disulphide, and other centro-symmetric molecules in chlorobenzene, nitrobenzene, benzonitrile, etc., reported signs that in such media the solutes, ordinarily non-polar, acquired apparent polarisations of considerable magnitude.

The actual numerical results were, however, computed by the conventional mixture formula, $P_{12} = P_1f_1 + P_2f_2$, where f and P represent molar fractions and molecular polarisation, and subscripts 1, 2, and 12, refer to solute, solvent, and solution, respectively. The Le Fèvre's commented at some length on the difficulty, inseparable from the application of this procedure to the systems indicated above, of estimating the contributions made by P_2 to the total polarisations of the solutions. It was clear that P_2 should not be taken as invariant with concentration, but rather as increasing in some manner with f_1. Nevertheless, an attempt to deduce " corrections " from the data of Pal (*Phil. Mag.*, 1930, **10**, 265) and Sutton and Jenkins (*J.*, 1935, 609) for benzene–nitrobenzene mixtures failed to eliminate the appearance of solute polarity in this one case, and strengthened the impression that the phenomenon was general.

During the intervening years several authors have adopted mathematical methods for extrapolating P_1 of a solute (in a non-polar solvent) to " infinite dilution " (cf. Le Fèvre, *Trans. Faraday Soc.*, 1950, **46**, 1, for refs.). In particular, equations showing ε_{12} and d_{12} as rectilinear with concentration of component 1 (cf. Hedestrand, *Z. physikal. Chem.*, 1929, *B*, **2**, 428; Le Fèvre and Vine, *J.*, 1937, 1805) are now known often to oversimplify—and thus misrepresent—relationships which really require extra terms involving the concentrations to powers higher than unity. In most instances when a wide composition range has not been covered, the introduction of f_1^2 (or w_1^2, *i.e.* the square of the weight fraction) provides adequate compensation (cf. Le Fèvre, *loc. cit.*), and $(\alpha\varepsilon_2)_{w_1}$ or $(\beta d_2)_{w_1}$ [calculated as $(\varepsilon_{12} - \varepsilon_2)/w_1$ or $(d_{12} - d_2)/w_1$, respectively] are found to have a straight-line dependence upon concentration. Their values at f_1 or $w_1 = 0$ can thus be obtained, and, when combined with directly determined constants for the pure solvent, yield the desired polarisation at infinite dilution. By following such a routine any inconstancy of P_2 need not mar the final figure for ${}_{\infty}P_1$.

The present work was intended to check the earlier findings of Le Fèvre and Le Fèvre by the method just outlined. Accordingly, we now report on solutions in nitrobenzene of benzene, *cyclo*hexane, naphthalene, decalin, diphenyl, and *p*-dichlorobenzene, using more solutions and a fuller choice of solutes than were taken in 1936. In each case equations to the curves between $(\alpha\varepsilon_2)_{w_1}$ or $(\beta d_2)_{w_1}$ and w_1 have been calculated from experimentally observed quantities, ${}_{\infty}P_1$ following therefore as $M_1[p_2(1 - \beta) + C\alpha\varepsilon_2]$, where α and β are the appropriate limiting coefficients and p_2 and C are as defined by Le Fèvre (*loc. cit.*). Our results are assembled in Table I together with, for comparison, the apparent moments * recorded by Le Fèvre and Le Fèvre.

TABLE I.

Apparent polarities of non-polar solutes in nitrobenzene.

Solute.	$(\alpha\varepsilon_2)_{w_1} = 0$.	$(\beta d_2)_{w_1} = 0$.	${}_{\infty}P_1$ (c.c.).	$[R_L]_D$ (c.c.).	μ, D.	μ, D.
Benzene	−67·2	−0·473	73·2	26·2	1·53	1·51 *
p-Dichlorobenzene	−42·7	+0·071	93·6	36·7	1·68	1·65 *
*cyclo*Hexane	−64·4	−0·692	91·1	27·7	1·78	—
Naphthalene	−51·3	−0·229	104·1	44·4	1·72	—
Decalin	−53·7	−0·467	132·6	44·1	2·10	—
Diphenyl	−51·7	−0·215	123·7	52·4	1·88	1·88 *

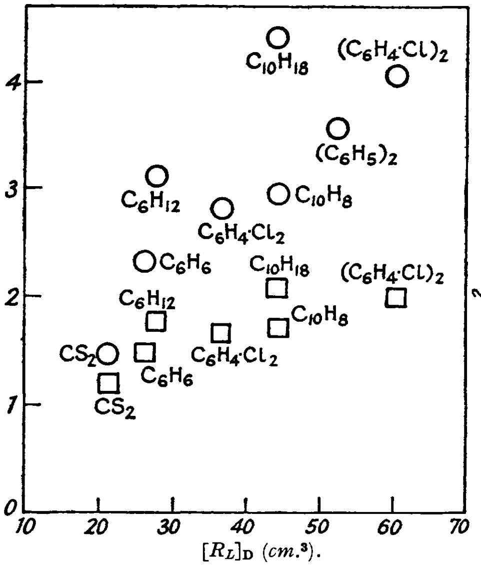
* See *J.*, 1936, 487.

In the three common cases the new determinations, made at 30°, confirm the older ones taken at 25°. For discussion, therefore, we will add the apparent moments previously observed in nitrobenzene of carbon disulphide (1·20 D.) and *pp'*-dichlorodiphenyl (2·00 D.).

DISCUSSION.

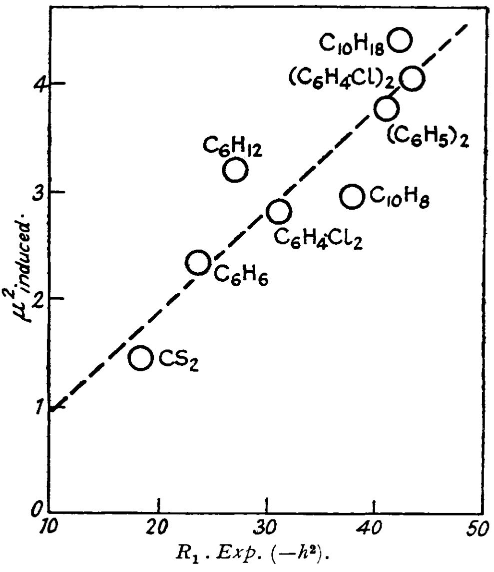
Le Fèvre and Le Fèvre (*loc. cit.*) noted that there was a rough proportionality between the induced moments and those of the solvent molecules. With the extended data now available, however, it becomes obvious that such a relationship is not exact. Fig. 1 shows μ_{induced} or μ^2_{induced} plotted against the molecular-refractivity values for the solutes; since $[R_L]_D =$

FIG. 1.



Plot of $\mu_{induced}$ (□) *and* $\mu^2_{induced}$ (○) *against the molecular refractivity.*

FIG. 2.



$4\pi N\alpha/3$, where α c.c. is the average polarisability, the non-rectilinearity of both curves indicates an absence of a direct dependence of μ_{induced} on α.

Intuitively it seemed that the anisotropy of polarisability of the dissolved molecules needed to be introduced. Of a number of attempts, the following has shown greatest promise : scale drawings of the structures concerned have been constructed with Stuart's " Wirkungsradien " (*Z. physikal. Chem.*, 1935, *B*, **27**, 350; cf. Barclay and Le Fèvre, *J.*, 1950, 556) superimposed, and lengths, A, B, or C, read off in three perpendicular directions set so that A is the greatest, and of B and C the second is the lesser. (In what follows, dimensions of solutes or solvents are denoted by suffixes 1 or 2.) A constant, h^2, could then be computed for each species *via* $h^2 = [(A - B)^2 + (B - C)^2 + (C - A)^2]/(A + B + C)^2$ and an indication of the departure from spherical symmetry provided by Exp. $(-h^2)$, which is of course unity when $A = B = C$. Fig. 2 shows the connection between μ^2_{induced} and $R_1 \,.\, \text{Exp.}(-h^2)$.

Empirical Formulæ for the Induced Moments.—By accepting the implications of Fig. 2, an equation (among others) such as $\mu^2_{\text{induced}} = (R_1/K)\text{Exp.}(-h^2)$ might apply. K would be a constant for the solvent, and indeed, by adopting a value of K of about 11 for nitrobenzene, a set of " calculated " values follow in reasonable agreement with experiment :

Solvent : nitrobenzene.

Solute :	CS_2.	C_6H_6.	$C_6H_4Cl_2$.	C_6H_{12}.	$C_{10}H_8$.	$C_{10}H_{18}$.	$(C_6H_5)_2$.	$(C_6H_4Cl)_2$.
$\mu_{\text{ind.}}$ (calc.)	1·3	1·5	1·7	1·6	1·7	2·0	1·9	2·0
$\mu_{\text{ind.}}$ (found)	1·2	1·5	1·7	1·8	1·7	2·1	1·9	2·0

For the five of these substances examined in chlorobenzene by Le Fèvre and Le Fèvre a K value of *ca.* 55 may be used, though less satisfactorily, possibly because the moments found were in all cases *less* than 1 D., so that squaring magnifies the effects of experimental errors :

Solvent : chlorobenzene.

Solute :	CS_2.	C_6H_6.	$C_6H_4Cl_2$.	$(C_6H_5)_2$.	$(C_6H_4Cl)_2$.
$\mu_{\text{ind.}}$ (calc.)	0·6	0·7	0·8	0·9	0·9
$\mu_{\text{ind.}}$ (found)	0·5	0·7	0·8	1·0	0·8

The two constants involved above (K = 11 or 55) correspond nearly to the reciprocal of $\mu^2_{\text{gas}}/A_2B_2C_2$. Accordingly we propose as a general equation :

$$\mu^2_{\text{induced}} = \mu_2{}^2_{\text{gas}} \,.\, R_1 \,.\, \text{Exp}(-h^2)/A_2B_2C_2,$$

and in Table II (last two columns) we show the concordance between calculation and measurement obtained for both solvents on this common basis.

TABLE II.

Solute.	Solvent.	A_1.	B_1.	C_1.	Exp.$(-h^2)$.	(μ_{induced}), calc.	found.
Benzene	Nitrobenzene	6·70	6·05	2·90	0·904	1·4	1·5
,, ...	Chlorobenzene	,,	,,	,,	,,	0·7	0·7
p-Dichlorobenzene ...	Nitrobenzene	9·46	6·05	3·16	0·843	1·6	1·7
,, ...	Chlorobenzene	,,	,,	,,	,,	0·8	0·8
*cyclo*Hexane	Nitrobenzene	6·71	5·42	4·50	0·974	1·5	1·8
Naphthalene	Nitrobenzene	8·98	7·18	2·90	0·851	1·8	1·7
Decalin	Nitrobenzene	7·94	6·71	4·50	0·951	1·9	2·1
Diphenyl	Nitrobenzene	10·96	6·05	2·90	0·779	1·8	1·9
,, ...	Chlorobenzene	,,	,,	,,	,,	0·9	1·0
Carbon disulphide ...	Nitrobenzene	6·40	3·08	3·08	0·869	1·2	1·2
,, ,, ...	Chlorobenzene	,,	,,	,,	,,	0·6	0·5
pp'-Dichlorodiphenyl	Nitrobenzene	13·68	6·05	3·16	0·713	1·9	2·0
,,	Chlorobenzene	,,	,,	,,	,,	0·9	0·8

The following solvent dimensions were used in the calculations : For nitrobenzene, A_2 = 8·00, B_2 = 6·05, C_2 = 4·50; for chlorobenzene, A_2 = 8·08, B_2 = 6·05, C_2 = 3·16. Refractivities used other than those listed elsewhere are as follows : For carbon disulphide, $[R_L]_D$ = 21·2 cm.³; for *pp'*-dichlorodiphenyl, $[R_L]_D$ = 60·5 cm.³.

EXPERIMENTAL.

Materials.—The nitrobenzene was purified by distillation, and had b. p. 208—210°/760 mm. The benzene was thiophen-free, and was purified as previously recorded (Earl, Leake, and Le Fèvre, *J.*, 1948, 2269). Commercial decalin presumably contained the *cis*- and *trans*-forms, and distilled continuously between 185° and 194°. The fraction of b. p. 189—190°/758 mm. was used, and assumed to contain equal parts of these forms. The remaining solutes were purified by distillation or recrystallisation, and had the boiling points or melting points recorded in the literature.

TABLE III.

10^6w_1.	ε^{30}.	d_4^{30}.	$(\alpha\varepsilon_2)_{w_1}$.	$(\beta d_2)_{w_1}$.
0	33·97	1·19828	—	—

Benzene, $M = 78{\cdot}11$.

10^6w_1.	ε^{30}.	d_4^{30}.	$(\alpha\varepsilon_2)_{w_1}$.	$(\beta d_2)_{w_1}$.
14,614	33·00	1·19135	−66·7	−0·474
19,197	32·69	1·18941	−66·5	−0·462
29,568	32·08	1·18462	−64·1	−0·462
37,678	31·59	1·18114	−63·2	−0·455
60,902	30·19	1·17132	−62·1	−0·443
83,446	28·95	1·16164	−60·2	−0·439
109,950	27·47	1·15060	−59·1	−0·434

whence $(\alpha\varepsilon_2)_{w_1} = -67{\cdot}2 + 78{\cdot}9w_1$; $(\beta d_2)_{w_1} = -0{\cdot}473 + 0{\cdot}392w_1$; $[R_L]_D = 26{\cdot}17$ cm.^{3} (from $n_4^{25} = 1{\cdot}49724$ and $d_4^{25} = 0{\cdot}87378$).

p-Dichlorobenzene, $M = 147{\cdot}01$.

10^6w_1.	ε^{30}.	d_4^{30}.	$(\alpha\varepsilon_2)_{w_1}$.	$(\beta d_2)_{w_1}$.
12,507	33·47	1·19908	−40·1	0·064
24,196	32·87	1·20013	−45·7	0·076
25,001	32·90	1·20014	−42·8	0·074
36,598	32·41	1·20106	−42·6	0·076
62,492	31·44	1·20301	−40·5	0·076
85,479	30·26	1·20415	−43·4	0·069
104,340	29·66	1·20620	−41·3	0·076

whence $(\alpha\varepsilon_2)_{w_1} = -42{\cdot}7 + 7{\cdot}67w_1$; $(\beta d_2)_{w_1} = = 0{\cdot}071$—$0{\cdot}024w_1$; $[R_L]_D = 36{\cdot}69$ cm.^{3} (from von Auwers, *Annalen*, 1921, **422**, 160).

*cyclo*Hexane, $M = 84{\cdot}16$.

10^6w_1.	ε^{30}.	d_4^{30}.	$(\alpha\varepsilon_2)_{w_1}$.	$(\beta d_2)_{w_1}$.
12,628	33·17	1·18951	−63·4	−0·694
21,398	32·60	1·18366	−64·3	−0·683
26,901	32·28	1·18011	−62·9	−0·675
32,324	31·94	1·17689	−62·8	−0·662
50,797	30·81	1·16462	−62·2	−0·663
76,796	29·37	1·14917	−60·0	−0·639
100,380	27·94	1·13373	−60·0	−0·643

whence $(\alpha\varepsilon_2)_{w_1} = -64{\cdot}4 + 48{\cdot}0w_1$; $(\beta d_2)_{w_1} = -0{\cdot}692 + 0{\cdot}577w_1$; $[R_L]_D = 27{\cdot}72$ cm.^{3} (from Landolt–Börnstein, "Tabellen," 1912, 1031).

Naphthalene, $M = 128{\cdot}16$.

10^6w_1.	ε^{30}.	d_4^{30}.	$(\alpha\varepsilon_2)_{w_1}$.	$(\beta d_2)_{w_1}$.
2,752	33·85	1·19765	−44·0	−0·229
6,841	33·60	1·19681	−54·4	−0·215
9,667	33·44	1·19625	−55·0	−0·210
24,303	32·77	1·19275	−49·3	−0·228
42,100	31·77	1·18857	−52·3	−0·231
74,229	30·17	1·18240	−51·2	−0·214
106,340	29·01	1·17853	−46·7	−0·186

whence $(\alpha\varepsilon_2)_{w_1} = -51{\cdot}3 + 23{\cdot}2w_1$; $(\beta d_2)_{w_1} = -0{\cdot}229 + 0{\cdot}272w_1$; $[R_L]_D = 44{\cdot}37$ cm.^{3} (from von Auwers and Frühling, *Annalen*, 1921, **422**, 192).

Decalin, $M = 138{\cdot}25$.

10^6w_1.	ε^{30}.	d_4^{30}.	$(\alpha\varepsilon_2)_{w_1}$.	$(\beta d_2)_{w_1}$.
12,444	33·34	1·19252	−50·9	−0·463
16,377	33·09	1·19066	−53·9	−0·465
20,537	32·84	1·18897	−55·1	−0·453
31,524	32·30	1·18365	−52·9	−0·464
47,659	31·40	1·17691	−53·9	−0·448
79,595	29·79	1·16329	−52·5	−0·440
109,910	28·33	1·15062	−51·3	−0·434

whence $(\alpha\varepsilon_2)_{w_1} = -53{\cdot}7 + 15{\cdot}9w_1$; $(\beta d_2)_{w_1} = -0{\cdot}467 + 0{\cdot}317w_1$; $[R_L]_D = 44{\cdot}1$ (calc. from Seyer and Barrow, *J. Amer. Chem. Soc.*, 1948, **70**, 802).

Diphenyl, $M = 154{\cdot}20$.

10^6w_1.	ε^{30}.	d_4^{30}.	$(\alpha\varepsilon_2)_{w_1}$.	$(\beta d_2)_{w_1}$.
12,115	33·35	1·19558	−50·8	−0·223
19,867	32·98	1·19428	−49·8	−0·201
21,865	32·88	1·19376	−49·8	−0·207
22,354	31·72	1·19379	−55·9	−0·201
32·951	32·34	1·19156	−49·5	−0·204
87,593	29·55	1·18065	−50·5	−0·201
101,370	29·01	1·17822	−48·9	−0·198

whence $(\alpha\varepsilon_2)_{w_1} = -51{\cdot}7 + 22{\cdot}6w_1$; $(\beta d_2)_{w_1} = -0{\cdot}215 + 0{\cdot}238w_1$; $[R_L]_D = 52{\cdot}41$ (from von Auwers and Frühling, *loc. cit.*).

Measurements.—The apparatus used was that described by Calderbank and Le Fèvre (*J.*, 1948, 1949) modified as noted by Le Fèvre and Northcott (*J.*, 1949, 333). Observations on 7 solutions of each solute are given in Table III. Symbols and the method of computation are explained in *Trans. Faraday Soc.*, 1950, **46**, 1. The dielectric constant measurements were made relative to nitrobenzene, ε for which at 30° has been taken from Ball (*J.*, 1930, 570).

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