116. *Solvent Effect in Dipole-moment Measurements. The Polarisations of Chloro- and Nitro-benzene, Chloroform, and Bromoform in a Series of Polar Solvents.*

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THE substances for which data have already been recorded (Le Fèvre and Le Fèvre, J., 1935, 1747) fall roughly into two classes, in one of which the total polarisation in the pure state is considerably less than, and in the other of which it is of the same order as, the total polarisation in the " infinitely dilute " (non-polar solvents) and/or the gaseous state. Molecules of compounds of these types were designated A and B respectively, and were distinguished by their Kerr constants. A very broad geometrical definition of the two groups was attempted, and a mechanism suggested whereby these factors could affect the observed polarisations.

The purpose of the present paper is to extend and illustrate the latter point by reference to two typical substances of each shape class, *viz.*, nitro- and chloro-benzene, both of type A (positive Kerr constants), and chloroform and bromoform, both of type B (negative Kerr constants).

Applicability of Existing Rules for Solvent Effects.—Several quantitative relations are extant connecting the polarisation of a solute with the dielectric constant of the medium and other factors (for references, see Goss, *Trans. Faraday Soc.*, 1934, **30**, 751; Frank, *Proc. Roy. Soc.*, 1935, **152**, 171). The majority are evidently of no general applicability for the reason implicitly stated before (Le Fèvre and Le Fèvre, *loc. cit.*), *viz.*, that the polarisations they forecast for substances in the vapour state are always higher than those in the liquid or dissolved condition (cf. *Trans. Faraday Soc.*, 1934, **30**, 860); *e.g.*, chloroform is a well-authenticated exception to this generalisation (*Nature*, 1935, **136**, 181), and certain amines behave in the same way. These rules considered only the *solvent.*

In certain other rules, *e.g.*, those of Weigle (*Helv. Physica Acta*, 1933, **6**, 68) and Frank (*loc. cit.*), (1) and (2) respectively,

$$\Delta\mu = A\mu^3 n(\alpha_1 - \alpha_2)^2/a^6 kT + B\mu n(\alpha_1 + 2\alpha_2)/3 \quad . \quad . \quad . \quad . \quad (1)$$

$$\Delta\mu = (A_1 + A_2)\mu(\varepsilon - 1)/\varepsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$${}_{O}P_{\text{liq.}} = {}_{O}P_{\text{gas}} + [(\varepsilon - 1)/(\varepsilon + 2)]N\Theta/3kT \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

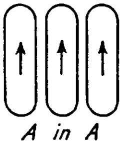
both solute and solvent properties are recognised, but the possibility (Le Fèvre and Le Fèvre, previous paper) that "non-polar" substances (such as benzene and carbon disulphide) can acquire considerable moments by dissolution in polar solvents markedly narrows the validity range, in as much as μ, the true moment in the gaseous state, is for these compounds zero, whence $\Delta\mu$ also should vanish.

Equation (3) (see Le Fèvre and Le Fèvre, *loc. cit.*) for the orientation polarisation of a substance in a medium of dielectric constant ε should, it is true, apply—by its derivation—only to pure substances and not to solutions. Nevertheless, it is obvious that a similar expression might be correct, for Θ can have either sign (depending ultimately on the shape of the molecule) and includes effectively such molecular properties as the polarisabilities of the compound along the three axes. The difficulty of evaluating Θ from *a priori* data, however, seriously limits the practical application of this equation at present; some calculations of Θ from Le Fèvre and Le Fèvre's experimental data show, moreover, that it varies with the solvent. Used in the manner required if (3) is to be applied to solutions, it cannot have the significance $\Theta = \Sigma\mu_1{}^2 s_1 + 2\Sigma\mu_1\mu_2 q_{12}$ given to it by Raman and Krishnan. It must presumably contain two terms at least, referring severally to the solute and the solvent molecules. The necessity for this is seen by considering two solutions : A in A and A in B. If A and B have the same dielectric constants, then in going from one to the other Θ must change its sign and value with the change of solvent. Similarly, for the pair A in A and B in A, the same change must accompany the change of type of solute. It would appear, therefore, that no equation for the polarisation of a substance in solution has yet been satisfactorily established.

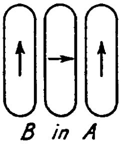
A Qualitative Treatment for the Solvent Effect.—The picture presented by Le Fèvre and Le Fèvre (*loc. cit.*) for the polarisation effects observed with *pure* liquids can be extended and utilised to predict correctly the results obtained when either polar or non-polar solutes are examined in polar or non-polar solvents. Those authors predicted that "a solvent of type A will be more effective in apparently reducing the orientation polarisation of a solute of its own type than in apparently increasing the corresponding polarisation of one of type B; again, a solvent of type B will cause smaller diminution of polarisation of an A type solute than it will an increase of polarisation of a solute of the second kind." The measurements now recorded were initiated to test this prediction. Their success justifies a more particular description than this quotation affords.

The tendency towards organised structures in liquids and solutions can be ascribed to forces of the van der Waals type operating between the molecules. The most stable structures will therefore be those in which the maximum number of atoms can make the closest possible approach; *i.e.*, where $E = \Sigma\,(-C/R^6)$ = a maximum — an expression for E, the mutual energy, of the type $E = -C/R^6 + be^{-R/S}$ being envisaged (cf. Born and Mayer, *Z. Physik*, 1932, **75**, 1; London, *Z. physikal. Chem.*, 1931, *B*, **11**, 222). The specifications of the molecular types A and B can be given, more accurately than was previously done, as those in which the principle moment lies roughly respectively *in*, or *at* 90° *to*, the *plane of greatest polarisability*. The latter will, in general, be the plane of greatest area.

The following procedure can be used to forecast the polarisation changes consequent upon dissolution, etc., of a substance. Imagine the solvent molecules aggregated about the solute so that the maximum number of atoms are in contact, and then consider the induction effects due to the moments in the solvent molecules on the solute unit so enclosed. Where aromatic compounds are under consideration especially, but probably generally, only two molecules of solvent to one of solute need be taken. Four arrangements suggest themselves for discussion, represented schematically as sections in (I), (II), (III), and (IV).



I



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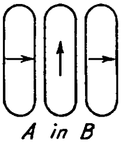
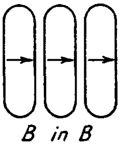
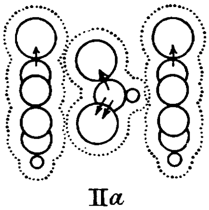


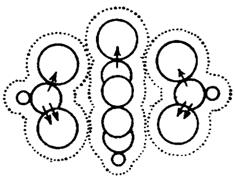
III



IV



IIa



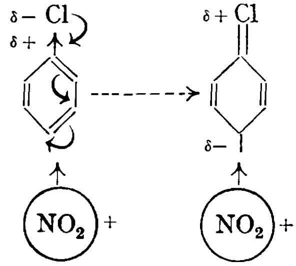
IIIa

Illustration of Method.—Chlorobenzene and nitrobenzene, either as pure liquids separately, or mutually dissolved, will conform to pattern (I). Because their polarisabilities are greatest along the length axis, considerable induction of moment in a reversed direction to the permanent resultant will be effected. A lowering of moment, and hence polarisation, will occur.

The induction will depend upon the polarisability of the solute, the moment of the solvent, and the distances between the molecules, etc. It is possible that in some cases the induced moment might outweigh the permanent moment; *e.g.*, *p*-dichlorobenzene in nitrobenzene acquires an induced moment of the order of that of chlorobenzene itself. In this connexion a calculation of the induced moment by the equation set out in the preceding paper is of interest. If R be taken as 3·5 Å. (Katz, *Z. angew. Chem.*, 1928, **41**, 329), μ as equal to the moments determined in the gaseous state, and α as the value derived from the molar refraction, then the orders of the induced moments are as in col. 5 :

Solute.	Solvent.	α_{solute}.	μ_{solvent}.	μ_{induced}.	$\mu_{\text{gas}}-\mu_{\text{induced}}$.
$PhNO_2$	$PhNO_2$	1·3	4·23	0·9	3·3
PhCl	PhCl	1·2	1·69	0·4	1·3
$PhNO_2$	PhCl	1·3	1·69	0·5	3·7
PhCl	$PhNO_2$	1·2	4·23	0·8	0·9

and the figures in col. 6 should correspond to the experimentally found values. These are 1·7, 1·2, 2·5, and 1·6, respectively, and, from their orders at least, afford some support to the views now advanced. The inversion of polarity of chlorobenzene by neighbouring polar nitrobenzene molecules is not without analogy to the electromeric polarisation generally assumed to occur prior to *p*-substitution when the essential part of a kationoid reagent approaches the *o*- or the *p*-nuclear position [cf. (V) and (VI)].



(V.) (VI.)

Chloro- and nitro-benzene dissolved in choroform are considered as in (III*a*), but owing to the tetrahedral dispositions of the C–Cl dipoles in the chloroform, they cannot, since induction varies as the cube of the distance, all three equally affect the most polarisable parts of the solute (*viz.*, the C–Cl or the $C-NO_2$ bond). For induction to lead to an *increase* of moment, the ratio between the distance of one C–Cl dipole of the chloroform molecule from the C–X of the solute to the (equal) distances of the other two C–Cl dipoles must be greater than $1/2^{\frac{1}{3}}$—the ratio for which neither increase nor decrease occurs. From the geometry of the chloroform molecule, it seems certain that the actual ratio must be smaller.

Nitro- and chloro-benzene should therefore show a slight reduction of moment in chloroform solution. The moments found are *ca.* 3·0 and 1·2 respectively. For analogous reasons, these solutes should show a reduction of polarisation in carbon disulphide, and, in fact, they do.

Solutions of chloroform and bromoform in chloro- and nitro-benzene can be considered on the basis of (II*a*). Here the dipoles of the solvents will (see above) reduce the nearest C–X dipole in the CHX_3 solute more than they will increase the other two. Since the resultant moments of chloroform and bromoform have the nature of a difference of three components, the net effect is to cause an increase. This is observed, particularly with nitrobenzene as solvent. It is of interest that the increases over the value in benzene (*viz.* 0·26 for chloro- and 0·38 for bromo-form) are in nearly the same ratio as the average polarisabilities of these molecules (*viz.*, 0·8 and $1{\cdot}2 \times 10^{-23}$ e.s.u.).

The effect of benzene as a solvent is to *raise* the polarisation of chloroform and lower those of chloro- and nitro-benzene compared with the gaseous values. This effect is most marked with the last solute. According to the qualitative picture described above, all three compounds should show higher moments in benzene solution (at infinite dilution) than in the vapour phase. This may really be the case, and pending further investigation we note that, for substances whose moments are between 1 and 4 as solutes, the weakest solution with which trustworthy observations can be made (say, *ca.* $f_1 = 0{\cdot}005$) corresponds to a number of solute molecules per c.c. roughly equal to that obtaining in the vapour of the substance at atmospheric pressure. For dipole-moment determinations in the gaseous state, the dielectric-constant estimations are generally made at pressures lower than this; hence, the minimum concentration for one method is roughly the maximum concentration for the other. In proportion, therefore, and in the same direction, as the P_1 is affected by mutual induction effects between the solute molecules, so will the estimated $^\infty P_1$ be correct, *i.e.*, the extrapolated polarisations for nitro- and chloro-benzene in solvents will always tend to be too low, whilst for chloroform, and generally for substances of the B shape class, the reverse should occur.

Results.—The measurements were made by methods set out before and are tabulated below under self-explanatory headings. The total polarisations at infinite dilution were calculated from the experimental figures, it being assumed that for dilute solutions both dielectric constant and density are linear functions of the concentration (Hedestrand, *Z. physikal. Chem.*, **1929**, *B*, **2**, 428), *i.e.*, that $\varepsilon_{\text{soln.}} = \varepsilon_{\text{solvent}} (1 + \alpha f_1)$ and $d_{\text{soln.}} = d_{\text{solvent}} (1 + \beta f_1)$, f_1 being the mol.-fraction of the solute; then $^\infty P_1 = A(M_1 - B\beta) + C\alpha$, where $A = (\varepsilon_2 - 1)/(\varepsilon_2 + 2)d_2$, $B = M_2/d_2$, and $C = 3M_2/[(\varepsilon_2 + 2)^2 d_2]$.

The values obtained by graphical estimation are included (in parentheses) for comparison.

Solute.	Solvent.	Total P_1, c.c.	Orientn. poln., c.c.	Apparent μ.
C_6H_5Cl	(gas)			1·69
	(liquid)	62	31	1·22
$[R_L]_D = 31$	C_6H_6	82·8 (82)	52 (51)	1·59 (1·57)
	$CHCl_3$	60·1 (61)	29 (30)	1·18 (1·20)
	$C_6H_5{\cdot}NO_2$	84·9 (84)	54 (53)	1·62 (1·60)
$C_6H_5{\cdot}NO_2$	(gas)			4·23
	(liquid)	94	61	1·72
$[R_L]_D = 33$	C_6H_6	371·7 (347)	339 (314)	4·05 (3·90)
	$CHCl_3$	225·2 (218)	192 (185)	3·05 (2·99)
	C_6H_5Cl	161·3 (158)	128 (125)	2·49 (2·46)
$CHCl_3$	(gas)			1·06
	(liquid)	45	24	1·10
$[R_L]_D = 21$	C_6H_6	52·1 (52)	31	1·22
	C_6H_5Me	52·6 (52)	32 (31)	1·24 (1·22)
	C_6H_5Cl	47·9 (48)	27	1·18
	$C_6H_5{\cdot}NO_2$	66·5 (67)	45·5 (46)	1·48 (1·49)
$CHBr_3$	(liquid)	47	17	0·91
	C_6H_6	52·9 (52)	23 (22)	1·06 (1·03)
$[R_L]_D = 30$	$CHCl_3$	45·0 (46)	15 (16)	0·85 (0·88)
	C_6H_5Cl	47·1 (48)	17 (18)	0·91 (0·93)
	$C_6H_5{\cdot}NO_2$	72·7 (73)	43	1·44

Solvent constants used.

Solvent.	A.	B.	C.
C_6H_6	0·3409	89·28	14·67
C_6H_5Me	0·3674	107·69	16·90
$CHCl_3$	0·3772	81·40	5·401
PhCl	0·5504	102·19	5·291
Ph·NO_2	0·7665	102·62	0·2262

Dielectric constant and density coefficients.

Solute.	Solvent.	α.	β.
C_6H_5Cl	C_6H_6	3·566	0·2578
,,	$CHCl_3$	0·6981	−0·4522
,,	$C_6H_5·NO_2$	−38·616	−0·0941
$CHCl_3$	C_6H_6	1·894	0·5384
,,	C_6H_5Me	1·6363	0·4798
,,	C_6H_5Cl	− 0·5243	0·3020
,,	$C_6H_5·NO_2$	−28·38	0·2372
$C_6H_5·NO_2$	C_6H_6	23·262	0·3782
,,	$CHCl_3$	31·44	−0·2931
,,	C_6H_5Cl	19·88	0·1024
$CHBr_3$	C_6H_6	1·7532	1·9749
,,	$CHCl_3$	− 0·6851	1·5218
,,	C_6H_5Cl	− 1·0236	1·5413
,,	$C_6H_5·NO_2$	−37·99	1·4442

Materials.—The substances used in this and the following investigation were commercially pure specimens, purified by redistillation immediately before use in order to remove small traces of moisture which greatly diminish the sharpness of the resonance curve in the dielectric-constant determination.

All determinations relate to 25°.

Chlorobenzene in benzene.

$f_1 . 10^6$	0	22973	57267	125128
ϵ	2·2725	2·3540	2·4790	2·7158
d	0·87370	0·87968	0·88848	0·90559
P_1	—	81·64	81·31	78·40

Chlorobenzene in chloroform.

$f_1 . 10^6$	0	21182	37554	83665
ϵ	4·7240	4·7381	4·7509	4·7836
d	1·46814	1·45836	1·45125	1·43090
P_1	—	60·30	60·27	59·75

Chlorobenzene in nitrobenzene.

$f_1 . 10^6$	0	35649	61809	106235
ϵ	34·89	33·490	32·539	30·796
d	1·19861	1·19526	1·19277	1·18865
P_1	—	84·38	84·47	83·72

Nitrobenzene in benzene.

$f_1 . 10^6$	0	34216	69472	70239
ϵ	2·2725	3·0537	3·9011	3·9239
d	0·87370	0·88667	0·89993	0·90025
P_1	—	314·9	281·8	281·6

Nitrobenzene in chloroform.

$f_1 . 10^6$	0	39602	62531	90352
ϵ	4·7240	5·9669	6·7001	7·5569
d	1·46814	1·45656	1·44979	1·44163
P_1	—	199·8	189·4	177·3

Nitrobenzene in chlorobenzene.

$f_1 . 10^6$	0	46199	70873	80073
ϵ	5·6120	6·5149	7·0275	7·2258
d	1·10085	1·10560	1·10808	1·10904
P_1	—	154·4	151·1	149·9

Chloroform in benzene.

$f_1 . 10^6$	0	65875	89280	147558	148847
ϵ	2·2725	2·3965	2·4406	2·5541	2·5557
d	0·87370	0·90894	0·92175	0·95336	0·95413
P_1	—	51·24	50·86	50·46	50·36

Chloroform in toluene.

$f_1 . 10^6$	0	140614	166891	225595
ϵ	2·3721	2·5997	2·6438	2·7471
d	0·85429	0·92112	0·93414	0·96386
P_1	—	50·86	50·60	50·20

Chloroform in chlorobenzene.

$f_1 . 10^6$	0	62172	96741	123919
ϵ	5·6120	5·5804	5·5588	5·5482
d	1·10085	1·11952	1·13006	1·13850
P_1	—	46·43	46·81	46·44

Chloroform in nitrobenzene.

$f_1 . 10^6$	0	92818	148910	264948
ϵ	34·890	32·250	30·673	27·372
d	1·19861	1·22028	1·23386	1·26256
P_1	—	66·81	66·58	66·11

Bromoform in benzene.

$f_1 . 10^6$	0	65880	116063
ϵ	2·2725	2·3881	2·4758
d	0·87370	1·00382	1·10290
P_1	—	51·24	50·73

Bromoform in chloroform.

$f_1 . 10^6$	0	20525	45276	56328
ϵ	4·7240	4·7107	4·6926	4·6838
d	1·46814	1·49939	1·53698	1·55373
P_1	—	45·10	44·81	44·68

Bromoform in chlorobenzene.

$_1 . 10^6$	0	26522	121695	124844
ϵ	5·6120	5·5850	5·4890	5·4819
d	1·10085	1·14132	1·28926	1·29433
P_1	—	48·34	48·24	48·03

Bromoform in nitrobenzene.

$f_1 . 10^6$	0	76036	150528	152577
ϵ	34·89	31·953	29·296	29·066
d	1·19861	1·30755	1·41776	1·41892
P_1	—	72·91	72·00	72·45

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