115. *The Apparent Dipole Moments of Benzene,* p-*Dichlorobenzene, Diphenyl,* 4 : 4′-*Dichlorodiphenyl, and Carbon Disulphide in Polar Solvents.*

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In this paper are recorded the dielectric constants and densities of solutions in a series of polar solvents of the substances indicated in the title. If the data so obtained can be treated in the usual manner for dipole-moment determinations, the results shown in the following table emerge. The figures under $\mu_{solv.}$ are the values for the solvent as a gas, where these are extant; the other headings have their usual significances. The apparent moments of the five solutes in the various solvents are given, as Debye units, in the penultimate column, and the ratios between the apparent moments of the solutes and the moments of the respective solvents are in the last column.

Solvent.	$_{T}^{\infty}P$, c.c.	$\epsilon_{solv.}$	$\mu_{solv.}$	$_{A}P + {}_{E}P$, c.c.	$_{O}P$, c.c.	$\mu_{app.}$	$\mu_{app.}/\mu_{solv.}$
(1) *Benzene as solute.*							
C_6H_6	27	2·27	0	27 *	0	0	—
$CHCl_3$	28	4·72 †	1·05	,,	1	*ca.* 0	—
C_6H_5Cl	38	5·61 ‡	1·69 §	,,	11	0·73	0·43
$C_6H_5{\cdot}NO_2$	73	34·89 †	4·23 §	,,	47	1·51	0·36
(2) p-*Dichlorobenzene as solute.*							
C_6H_6	38	2·27	0	38 **	0	0	—
CCl_4	37	2·23	0	,,	0	0	—
$C_6H_5{\cdot}NMe_2$	48	4·85 ‖	1·6	,,	10	0·70	0·44
C_6H_5Cl	52	5·61	1·69	,,	14	0·82	0·49
$C_6H_5{\cdot}CO_2Et$	53	5·77 ‖	1·8—1·9	,,	15	0·85	0·44
$C_6H_5{\cdot}CN$	91	25·20 †	4·39	,,	53	1·60	0·36
$C_6H_5{\cdot}NO_2$	94	34·89	4·23	,,	56	1·65	0·39
(3) *Diphenyl as solute.*							
C_6H_6	50	2·27	0	50 ¶	0	0	—
C_6H_5Cl	69	5·61	1·69	,,	19	0·96	0·57
$C_6H_5{\cdot}NO_2$	123	34·89	4·23	,,	73	1·88	0·44
(4) 4 : 4′-*Dichlorodiphenyl as solute.*							
C_6H_6	66	2·27	0	63 ¶	3	*ca.* 0	—
C_6H_5Cl	77	5·61	1·69	,,	14	0·82	0·48
$C_6H_5{\cdot}NO_2$	146	34·89	4·23	,,	83	2·00	0·47
(5) *Carbon disulphide as solute.*							
CS_2	21	2·64	0	21 ¶	0	0	—
C_6H_6	23	2·27	0	,,	2	*ca.* 0	—
C_6H_5Cl	26	5·61	1·69	,,	5	0·49	0·29
$C_6H_5{\cdot}NO_2$	51	34·89	4·23	,,	30	1·20	0·28

* Errera (*Bull. Acad. roy. Belg.*, 1926, 327).

† Ball (J., 1930, 570).

‡ Sugden (J., 1933, 772).

§ Groves and Sugden (J., 1934, 1094).

‖ Present work.

¶ The $[R_L]_D$ value.

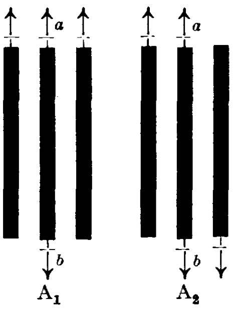
** *I.e.*, the distortion polarisation, taken as 38 c.c. from the measurements of Smyth, Morgan, and Boyce (*J. Amer. Chem. Soc.*, 1928, **50**, 1536) and Errera (*Compt. rend.*, 1936, **182**, 1623; *Physikal. Z.*, 1926, **27**, 764; " Polarisation Diélectrique," Paris, 1928) on the *solid* substance.

The induced moment of the solute is throughout roughly proportional to the *moment*, rather than the dielectric constant, of the solvent (see last column of table); the latter constant certainly does not have, in these measurements, the large influence indicated by the various empirical and *a priori* equations hitherto advanced.

Discussion.—These results are qualitatively in agreement with a suggestion previously outlined by us (J., 1935, 1747); this depended on the occurrence of regular (graphite-like) units of structure in the liquids, for which (notably aromatic compounds) there seems to be independent physical evidence (cf. Katz, *Z. angew. Chem.*, 1928, **41**, 329; Stewart, *Indian J. Physics*, 1932—3, **7**, 603). The underlying cause of this we suppose to be the operation of van der Waals forces. According to the theories of London (*Z. Physik*, 1930,

63, 245; *Z. physikal. Chem.*, 1931, **11**, *B*, 222), the reciprocal binding energy due to such forces between two atoms at a distance R apart is $E = -C/R^6$, which is approximately equal to $-1{\cdot}36n^{1/2}\alpha^{3/2}\alpha_0^{3/2}E_0/R^6$ (cf. Slater and Kirkwood, *Physical Rev.*, 1931, **37**, 682), in which n is the number of electrons in the outermost shell of the atomic species under consideration. Now, the reciprocal energy of any one atom with respect to a system of others can be obtained by addition of the reciprocal energies with respect to each of these atoms individually. Thus, the reciprocal energy for two molecules is obtained by summation of the mutual energies of all the centres of the first molecule with those of all the centres of the second molecule. The influence of an inverse R^6 term is to make two molecules effecting mutual orientation do so in such a manner that the greatest number of atoms (*i.e.*, giving the largest possible value for n) are in the closest possible approach to one another, thus allowing the maximum achievable intermolecular attractive force to become operative (where aromatic molecules are concerned this will mean practically that association will occur so that surfaces of greatest area are in contact).

Where the solute is non-polar by virtue of exact coaxial apposition of two strong dipoles well removed from each other, and the solvent has molecular dimensions roughly equal to those of the solute but differs in having only one large dipole, the following possibilities arise (illustrated by particular reference to *p*-dichlorobenzene in chlorobenzene solution). At considerable dilutions each *p*-dichlorobenzene molecule will be included between two aggregates of solvent molecules; it, together with its immediate neighbours, could be imagined as approaching either of the two extreme configurations shown sectionally as A_1 and A_2.



Obviously, the effect on the resultant moment of the solute will be different in the two cases. In A_2, equal but opposite induced moments will be set up in counteraction to the two permanent moments *a* and *b* : the net effect will therefore be zero. In this respect this configuration for the solvent molecules, among the infinitude possible between A_1 and A_2, is unique. In A_1, on the other hand, the effective moment indicated at *a* will be lowered whilst that at *b* will (at least) remain as before; the net resultant moment will therefore be finite.

The experimental results appear to indicate that the A_1 type of aggregation is favoured, *i.e.*, that the dipolar solvent units cluster around the solute with their dipoles in parallel rather than antiparallel alinement.

In this way the proportionality of the induced and the inducing dipoles is explained. It is interesting, therefore, to make an estimate of the polarisability, α, of the solute molecules on the basis of the model described in the diagram A_1. The expression $\mu_{\text{induced}} = 2\alpha F$, where $F = (\mu/\varepsilon r^3)(\varepsilon + 2)/3$, should be applicable. In the case, *e.g.*, of *p*-dichlorobenzene in nitrobenzene, the experimentally measured value of μ_{induced} is 1·65. If r (the distance between two molecules in A_1) be taken as *ca.* 3 Å., μ (the moment of nitrobenzene) as 4, and $(\varepsilon + 2)/\varepsilon$ be regarded as unity for large values of ε ($\varepsilon_{\text{PhNO}_2}$ is *ca.* 35), we have $\alpha = 1$—2×10^{-23} e.s.u. Values of the same order are derivable for α from the results for the other solutions studied in this paper :

Solvent.	C_6H_6.	Ph·Ph.	*p*-$C_6H_4Cl_2$.	*pp'*-$C_6H_4Cl{\cdot}C_6H_4Cl$.
C_6H_5Cl	1·29	1·70	1·45	1·45
$C_6H_5{\cdot}NO_2$	1·37	1·70	1·49	1·81

Comparison with the experimental results of Stuart and Volkmann (*Z. Physik*, 1933, **80**, 107) is satisfactory. These authors, from measurements of the Kerr effect, give the polarisability of the benzene ring in its plane as $1{\cdot}23 \times 10^{-23}$, and the average polarisability of a benzene molecule as $1{\cdot}03 \times 10^{-23}$. In addition, it is noteworthy that the average polarisabilities (derived from the molecular refractivities $[R_L]_D$) of the molecules in question are : benzene, 1·03; diphenyl, 1·97; *p*-dichlorobenzene, 1·42; 4 : 4'-dichlorodiphenyl, 2·48. It is clear, therefore, that our results are reasonably explained by the physical picture to which allusion has been made. If the average polarisabilities are divided into the three components in each case, it will be noticed that with benzene and its *p*-dichloro-derivative the agreement is good between our experimental α value and the calculated figure for the greatest axis of length, but with the diphenyl compounds the result found is too small. This may be due to the fact that the polarisable parts of the solute molecules are more remote from the polarising solvent units, or it may arise from a tendency for the solvent molecules to associate symmetrically in groups of four around a solute of the diphenyl type so that all induction effects are, in the resultant, cancelled out. The observed μ_{induced} for these compounds should therefore be smaller than would be the case if the simple arrangement assumed for the above calculations were to occur uniformly throughout the solutions.

Possible Alternative Explanations.—In the calculation of our results from the actual measurements of d and ε, etc., we have divided the observed total polarisations of the solutions into P_1f_1 and P_2f_2 by a simple mixture formula. This treatment when the solvent is non-polar—or practically so—is usually correct to the order of experimental accuracy. The solvent in such cases greatly preponderates, and its polarisation is independent of the concentration. The objection may be raised that this condition does not obtain in our experiments. To quote three examples: the values of P_2 for chlorobenzene, benzonitrile, and nitrobenzene as pure liquids are 61, 92, and 64 c.c., but as solutes at infinite dilution in the common non-polar solvents they are 80—85, 300—360, and 350—370 c.c. respectively; their polarisations (and those of all polar liquids of type A—see Le Fèvre and Le Fèvre, *loc. cit.*) are markedly affected by the dilution. In our measurements, while the concentration of the solute is becoming greater (*i.e.*, as f_1 is increasing) the solvent is becoming more dilute. Accordingly, its P_2 should be increasing, and our measured $P_1f_1 + P_2f_2$ might therefore contain the effect of this higher polarisation. Since from this (experimental) result we subtract P_2f_2 calculated on the basis of P_2 for the pure solvent (and this is liable to be for each solution erroneously small), P_1f_1—and hence P_1—may appear incorrectly large.

However, we are of the opinion that this effect is not present sufficiently to invalidate the conclusions previously stated. It will be noticed that P_1 shows throughout a tendency to rise as f_1 decreases. If P_2 were diminishing in the way described at the same time the reverse order for the P_1 figures would be expected. The apparent insensitiveness of P_1 to changes in f_1, however, may very likely be in some cases due to the superimposition of the (normal) P_{solute} increase and this (polar) solvent effect (decrease of P_2) with diminution of f_1.

The errors produced by inconstancy of P_2 should clearly become greater as f_2 diminishes; extrapolation, therefore, of P_1 (apparent) back to $f_1 = 0$ should furnish a value of ${}_{\infty}P_1$ free from uncertainties of the type under examination; in no case, however, has this process indicated a value approaching that appropriate for the substance in, *e.g.*, benzene solution.

A priori estimation of the significance of this effect in our solutions is difficult because either P_1 or P_2 has to be assumed constant (or at least its variation with concentration must be known) before the observed polarisation of the solution can be analysed into its component factors. Pal (*Phil. Mag.*, 1930, **10**, 265) and Sutton and Jenkins (J., 1935, 609) have studied the changes of polarisation of benzene–nitrobenzene mixtures with variation of f_1 and f_2, and have calculated the P_{PhNO_2} on the assumption of a fixed polarisation for benzene throughout—just the assumption the validity of which we are now led to question. If, *e.g.*, Pal's conclusions are used as a basis for correction of our results, it is observed that for dilute solutions of benzene in nitrobenzene, the P_{PhNO_2} is nearly linear with concentration. From a curve, " corrected " values of P_2 can be read off and used in the tables given later. In this way, the final P_1 is admittedly lowered in all cases where the method has been tried; the exaltation over the polarisation figure corresponding to $\mu = 0$, however, does not seem to be entirely eliminated even by this treatment.

Lastly, it might be urged, in criticism of our view, that in chloroform solution benzene appears to be practically non-polar, and that this solvent is one whose polarisation is almost the same whether measured in the liquid, dissolved, or gaseous state (Le Fèvre and Le Fèvre, *loc. cit.*), and is therefore one whose polarisation contribution should be calculable accurately for all concentrations. Our difficulty here is that nothing *a priori* can certainly be said regarding the structure of the solutions; but, if a similar argument to that developed for the aromatic liquids may be used, we should not expect any marked change in the moment of the solute, an expectation which is in agreement with the experimental results.

EXPERIMENTAL.

Materials.—A commercial " pure " specimen of *p*-dichlorobenzene was recrystallised several times from alcohol; m. p. 52—53°. We are indebted to Dr. E. E. Turner for gifts of pure diphenyl and its 4 : 4′-dichloro-derivative. The various liquids were purified by usual methods, and when used as solvents, were always redistilled prior to use to remove traces of moisture which, when present, seriously disturb the dielectric-constant measurements. The b. p.'s were those recorded in the literature in all cases save that of *o*-dichlorobenzene : this boiled steadily over a small range (172—178°) and may therefore have contained some *p*-isomeride as an impurity. The density observed, however, is in good agreement with that given by Philip (J., 1912, **101**, 1868).

Method.—The dielectric constants and densities of the solutions at 25° were determined by the resonance method (J., 1935, 480), and the polarisations of the solutes calculated as indicated above.

The significant data for 25° are collected in the following tables, in which the symbols P and f refer respectively to the molecular polarisation and the molar fraction of the components in the solutions, the subscripts 1 and 2 applying to solute and solvent respectively; ε and d denote the dielectric constant and density of the solutions.

p-*Dichlorobenzene in benzene.*

$f_1 . 10^6$ ...	0	13297·0	14652·1	17856·0	33306·0
ϵ	2·2725	2·2756	2·2759	2·2767	2·2803
d	0·87368	0·88063	0·88127	0·88293	0·89090
$P_1f_1+P_2f_2$	26·5900	26·7361	26·7527	26·7889	26·9596
P_1	—	37·58	37·69	37·73	37·69

p-*Dichlorobenzene in carbon tetrachloride.*

$f_1 . 10^6$	0	10699	14069·6	22696·2	394020
ϵ	2·2287	2·2319	2·2329	2·2354	2·2405
d	1·58454	1·58143	1·58045	1·57791	1·57299
$P_1f_1+P_2f_2$	28·2395	28·3335	28·3630	28·4383	28·5888
P_1	—	37·02	37·02	37·00	37·10

p-*Dichlorobenzene in dimethylaniline.*

$f_1 . 10^6$ ...	0	44001·0	51991·6	72904·1	90001·9
ϵ	4·8495	4·7558	4·7450	4·7007	4·6635
d	0·95198	0·96515	0·96746	0·97390	0·97918
$P_1f_1+P_2f_2$	71·4336	70·3563	70·2176	69·6923	69·2525
P_1	—	46·95	48·04	47·55	47·20

p-*Dichlorobenzene in chlorobenzene.*

$f_1 . 10^6$	0	20014·7	29997·9	36663·5	52707·2
ϵ	5·6120	5·5463	5·5126	5·4894	5·4398
d	1·10085	1·10489	1·10687	1·10822	1·11140
$P_1f_1+P_2f_2$	61·9177	61·7184	61·6125	61·5351	61·3829
P_1	—	51·96	51·74	51·48	51·77

p-*Dichlorobenzene in ethyl benzoate.*

$f_1 . 10^6$	0	43998·2	58980·9	72903·0
ϵ	5·7658	5·6546	5·6151	5·5729
d	1·04446	1·05309	1·05580	1·05882
$P_1f_1+P_2f_2$	88·1351	86·5373	86·0009	85·4211
P_1	—	51·82	51·95	50·0

p-*Dichlorobenzene in* o-*dichlorobenzene.*

$f_1 . 10^6$	0	20012·0	31332·7	39245·2
ϵ	6·8281	6·7348	6·6835	6·6426
d	1·29381	1·29360	1·29347	1·29342
$P_1f_1+P_2f_2$	75·0077	74·6078	74·3847	74·2016
P_1	—	55·03	55·12	54·48

p-*Dichlorobenzene in benzonitrile.*

$f_1 . 10^6$ ...	0	52555·3	105778·6	120998·9
ϵ	25·200	23·822	22·561	22·111
d	1·00088	1·01734	1·03373	1·03841
$P_1f_1+P_2f_2$	91·5593	91·4907	91·4213	91·3376
P_1	—	90·25	90·26	89·73

p-*Dichlorobenzene in nitrobenzene.*

$f_1 . 10^6$	0	28201·0	43975·9	76563·1	95651·0
ϵ	34·890	33·501	32·723	31·182	30·239
d	1·19852	1·20122	1·20265	1·20553	1·20759
$P_1f_1+P_2f_2$	94·2807	94·2588	94·2397	94·1917	94·1017
P_1	—	93·50	93·35	93·12	92·41

Benzene in chloroform.

f_1	0	0·036524	0·057436	0·140865
ϵ	4·7240	4·5779	4·4919	4·1630
d	1·46814	1·44409	1·43029	1·37624
$P_1f_1+P_2f_2$	45·0799	44·4397	44·0437	42·3836
P_1	—	27·55	27·04	25·94

Benzene in chlorobenzene.

f_1	0	0·073737	0·106258	0·190284
ϵ	5·6120	5·3775	5·2789	5·0111
d	1·10085	1·08562	1·07929	1·06190
$P_1f_1+P_2f_2$	61·9177	60·0977	59·2780	57·0735
P_1	—	37·24	37·07	36·46

Benzene in nitrobenzene.

f_1	0	0·050997	0·057915	0·106981
ϵ	34·89	32·853	32·630	30·783
d	1·19861	1·18427	1·18232	1·16834
$P_1f_1+P_2f_2$	94·2736	93·1505	93·0072	91·9000
P_1	—	72·25	72·41	72·09

Diphenyl in benzene.

f_1	0	0·005201	0·008689	0·012111
ϵ	2·2725	2·2754	2·2774	2·2794
d	0·8738	0·87561	0·87679	0·87805
$P_1f_1+P_2f_2$	26·5850	26·7085	26·7922	26·8716
P_1	—	50·33	50·43	50·25

Diphenyl in chlorobenzene.

f_1	0	0·004019	0·010544	0·034602
ϵ	5·6120	5·5943	5·5642	5·4469
d	1·10085	1·10036	1·09975	1·09734
$P_1f_1+P_2f_2$	61·9177	61·9432	61·9650	62·0015
P_1	—	68·26	66·40	64·34

Diphenyl in nitrobenzene.

f_1	0	0·014801	0·033482	0·052476
ϵ	34·89	33·874	32·681	31·280
d	1·19861	1·19481	1·19025	1·18465
$P_1f_1+P_2f_2$	94·2736	94·6889	95·1971	95·7180
P_1	—	122·30	121·86	121·80

4 : 4′-*Dichlorodiphenyl in benzene.*

f_1	0	0·005208	0·011346	0·024588
ϵ	2·2725	2·2772	2·2826	2·2939
d	0·87380	0·87789	0·88271	0·89273
$P_1f_1+P_2f_2$	26·5850	26·7879	27·0225	27·5318
P_1	—	65·53	65·14	65·09

4 : 4′-*Dichlorodiphenyl in chlorobenzene.*

f_1	0	0·006127	0·006894	0·011645
ϵ	5·6120	5·5773	5·5735	5·5472
d	1·10085	1·10262	1·10283	1·10422
$P_1f_1+P_2f_2$	61·9177	62·0051	62·0193	62·0860
P_1	—	76·18	76·65	76·37

4 : 4′-*Dichlorodiphenyl in nitrobenzene.*

f_1	0	0·009777	0·015007	0·024373
ϵ	34·89	34·1693	33·7798	33·0900
d	1·19861	1·19966	1·20027	1·20129
$P_1f_1+P_2f_2$	94·2736	94·7722	95·0302	95·4915
P_1	—	145·27	144·69	144·24

Carbon disulphide in benzene.

f_1	0	0·021799	0·040002	0·074353	0·169211
ϵ	2·2725	2·2789	2·2842	2·2941	2·3194
d	0·8738	0·87901	0·88332	0·89158	0·91573
$P_1f_1+P_2f_2$	26·5850	26·5071	26·4420	26·3149	25·9055
P_1	—	23·01	23·01	22·95	22·57

Carbon disulphide in chlorobenzene.

f_1	0	0·121411	0·125168	0·172855
ϵ	5·6120	5·3596	5·3479	5·2478
d	1·10085	1·11180	1·11193	1·11641
$P_1f_1+P_2f_2$	61·9177	57·5792	57·4363	55·7468
P_1	—	26·18	26·12	26·22

Carbon disulphide in nitrobenzene.

f_1	0	0·108787	0·174559	0·183080
ϵ	34·89	32·191	30·507	30·278
d	1·19861	1·20081	1·20246	1·20274
$P_1f_1+P_2f_2$	94·2736	89·5589	86·6568	86·2722
P_1	—	50·94	50·64	50·57

The comparison between benzene and carbon disulphide seemed of particular interest from the point of view discussed above (p. 489). The molecular weights of these two solutes are very nearly identical, and if the polarisation effects now reported are ascribable to P_2 changes—rather than to induction in the solute molecules—then at the same concentrations in, *e.g.*, nitrobenzene these two substances should exhibit nearly the same apparent polarisations. Inspection of the tables shows that they do not do so, either in nitro- or in chloro-benzene solution.

SUMMARY.

(1) The typical non-polar substances named in the title become apparently polar when dissolved in polar solvents.

(2) The degree of apparent polarity so induced varies roughly directly with the moment of the solvent.

(3) These observations can be harmonised with a qualitative picture previously given.

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[*Received, December 20th,* 1935.]