110. *The Molecular Polarisations of Nitrobenzene in Various Solvents at 25°.*

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A SYSTEMATIC investigation of the molecular electrical polarisations of nitrobenzene in various solvents at 25° has been made, in order to obtain information as to the validity of the dilute solution method of measuring electrical dipole moments. Although this method avoids the influence of dipole association, it cannot avoid the influence of solute on solvent and *vice versa* (see preliminary note, *Nature*, 1934, **133**, 106).

Horst Müller (*Physikal Z.*, 1932, **33**, 731) measured the polarisation of chlorobenzene in non-polar solvents, and Fairbrother (J., 1933, 1541) that of hydrogen chloride in benzene, ethyl bromide, and ethylene dichloride. Otherwise, but little systematic work on the influence of the solvent has been done, although Smallwood (*Z. physikal. Chem.*, 1932, *B*, **19**, 242) has discussed theoretically the errors in dipole moment data due to the neglect of atom polarisation and the influence of the solvent. Some work of an entirely different kind, *e.g.*, Bell's solubility and partition coefficient determinations (J., 1931, 1371; *Trans. Faraday Soc.*, 1931, **27**, 797), indicates that the dipole field plays an important part in solvents of low dielectric constant and that there is some interaction between dipole molecules and solvent molecules.

Nitrobenzene has now been studied in non-polar solvents and in chloroform; this solute was chosen since it has a fairly large dipole moment and is easily prepared pure. Previous investigators, *e.g.*, Williams (*Physikal. Z.*, 1928, **29**, 174), have found that, within the limits of their accuracy, the total polarisation at infinite dilution is independent of the non-polar solvent taken.

EXPERIMENTAL.

Materials.—Benzene. Hopkin and Williams's thiophen-free material was frozen out four times, refluxed over phosphoric oxide, and distilled in a current of dry air into a receiver from which it could be transferred when required by the use of pneumatic pressure.

Carbon tetrachloride. Albright and Wilson's product was refluxed and distilled over phosphoric oxide in a current of dry air.

Decalin. Hopkin and Williams's commercial decalin (decahydronaphthalene) was stirred for 12 hours with concentrated sulphuric acid, and then with potassium permanganate for a further 6 hours. This last process produced a colloidal solution of the reagent in decalin, and so the solution was stirred with acidified ferrous sulphate until colourless. The material was then washed several times with water and fractionally distilled over phosphoric oxide, a mixture of the *cis*- and the *trans*-form being obtained; b. p. 190—193°.

cyclo*Hexane.* Chemical methods of purification together with fractional distillation failed to give a good product, and so the compound was synthesised from benzene and hydrogen by passing the mixed gases over a reduced nickel catalyst deposited on small sieved pumice stones. The product was analysed by density and freezing-point determinations. With the conditions used, which were the result of numerous trials and gave at least a 90% yield, the material obtained generally had f. p. – 3·0°, $d_{4^\circ}^{25^\circ}$ 0·77 (I.C.T. give f. p. 6·5°; $d_{4^\circ}^{25^\circ}$ 0·774). The impurities present were unchanged benzene and probably some dihydrobenzenes and tetrahydrobenzene (potassium permanganate was decolorised). These were removed by shaking with concentrated sulphuric acid, then with potassium permanganate, and washing five times with water. Fractional distillation from phosphoric oxide through a 4-foot column gave a product of f. p. 6·45° ± 0·02°.

n-*Hexane.* B.D.H. Material "free from aromatic hydrocarbons" was heated gently on the water-bath with fuming nitric acid for 6 hours, then fractionally distilled over phosphoric oxide, the fraction of b. p. 66·8—67·5°/760 mm. being collected.

Carbon disulphide. A commercial sample was fractionally distilled over ceresin; b. p. 45·8°/758 mm.; its dielectric constant at 25° coincided with that given by Williams and Ogg (*J. Amer. Chem. Soc.*, 1928, **50**, 94).

Chloroform. Hopkin and Williams's material was shaken with concentrated sulphuric acid, then with potassium hydroxide solution, washed several times with water, and fractionally distilled from phosphoric oxide through a 4-foot column.

Nitrobenzene. This was prepared from pure thiophen-free benzene (see above) by nitration below 40° (Sidgwick and Ewbank, J., 1924, **125**, 2268). It was distilled under reduced pressure below 100°, and a portion redistilled for each series of measurements, the f. p. always being checked (5·69°).

Measurement of Dielectric Constants.—Dielectric constants were measured by a heterodyne-beat method at a wave-length of 500 m., with the apparatus described by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668). Some modifications were made in the lay-out to minimise lead inductance, obtain better switching, etc., and two single-solution platinum-plated brass cells were constructed of air capacities 25 μμF and 80 μμF, the former being used for the work with chloroform. Also, a thermionic-valve-maintained tuning fork was used to match the heterodyne note. All apparatus will be more fully described in a future communication. The platinum-plated cells were calibrated with pure benzene at 25°, the corresponding dielectric constant of benzene being taken as 2·2727 (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 664).

On account of the use of chloroform, it was thought desirable to test the cell full of polar liquid for dielectric loss. The heterodyne-beat method consists in principle in adjusting a capacity C_A to equal a capacity C_B. Now C_A consists of a number of air condensers assumed perfect, whilst C_B has included in it the cell capacity. If there is dielectric loss on the B side of the circuit, then the condenser reading on the A side of the circuit will not correspond to the true capacity of the B side, and error in the measured dielectric constant results. The orders of magnitude of the equivalent resistances involved were therefore determined. (I thank Mr. W. Jackson, and Mr. F. C. Frank of the Engineering Laboratory, University of Oxford, for loan of apparatus, advice, and assistance in connexion with these resistance measurements.)

A tuned grid oscillator was constructed, giving a wave-length of 500 m., *i.e.*, the wave-length at which the dielectric constants were measured. A pick-up circuit loosely coupled to the oscillator consisted of an inductance of small resistance in series with which could be placed known small resistances of fine eureka wire, their high-frequency and direct-current resistance being identical. The circuit also contained two calibrated variable capacities for coarse and fine tuning, and it was also possible to put the liquid condenser or cell in and out of the circuit. Across one of the capacities was a Moullin thermionic voltmeter. The usual resonance method of measuring a condenser resistance was then applied.

Some specimen results are given. The total circuit capacity at resonance was about 550 $\mu\mu$F. The circuit resistance was found to be 2·07 ohms whether the cell with air as dielectric was included in the circuit or not. The equivalent series resistance of the cell with air as dielectric is thus zero. Specimen solutions in the cell gave equivalent series resistances of 0·04 ohm and 0·20 ohm. Now the following two circuits are equivalent to one another; (*a*) a capacity C shunted by a high resistance R, (*b*) a capacity C_c in series with a small resistance r. By applying the usual method using symbolic impedances (see Hague, " A.C. Bridge Methods "), it can be shown that

$$r = R/(1 + R^2C^2\omega^2) \simeq 1/RC^2\omega^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where r is the measured equivalent series resistance and R the parallel resistance; also

$$C_c = C + 1/R^2C\omega^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The correction to the heterodyne-beat method capacity is thus $1/R^2C\omega^2$. Insertion of the values $r = 0{\cdot}2$ ohm, $C = 550\ \mu\mu\mathrm{F}$, $f = \omega/2\pi = 600$ kc. in equation (1), gives $R =$ *ca.* 10^6 ohms; by inserting this value of R in equation (2), together with $C = 200\ \mu\mu\mathrm{F}$ (say) and $f = \omega/2\pi = 600$ kc., it is seen that the correction to be applied to a measured capacity of 2×10^{-10} farad is about 10^{-16} farad and hence unimportant. This resonance method is being applied to solvents of higher dielectric constant.

Measurement of Densities.—The usual Sprengel–Ostwald pyknometer was used.

Measurement of Refractive Indices.—These were measured with the Pulfrich type of instrument for the Hg green line 5461, a centrally divided cell being used. The refractivities were calculated with the usual Lorenz–Lorentz formula and were not extrapolated to infinite wave-length. Measurements were made in benzene and carbon tetrachloride, and ${}_{\mathrm{E}}P_2$, the electron polarisation of nitrobenzene, found to be 32·6 c.c.

The results are in the following tables; f_2 is the molecular fraction of nitrobenzene, $\varepsilon_{25°}$ the dielectric constant, $d^{25°}_{4°}$ the density, P_{12} the molecular polarisation of the mixture, P_2 that of the solute, ${}_{\infty}P_2$ the total polarisation of the solute at infinite dilution, and $P_{\mathrm{A+O}}$ is the atom + orientation polarisation. The apparent dipole moment μ is calculated by the usual Debye equation $\mu = \sqrt{9kTP_{\mathrm{A+O}}/4\pi N}$, the unknown atom polarisation being included. The relative accuracy in $\varepsilon_{25°}$ is considered to be $\pm$ 0·0002, except for chloroform solutions, where the error is probably $\pm$ 0·0008. Polarisations of solute are calculated from differences and so it is unnecessary to know the absolute value of the dielectric constant. The densities are correct to the fourth place of decimals, and ${}_{\infty}P_2$ is subject to an error of 0·5—1·0 c.c.

Apparent Dipole Moments of Nitrobenzene at 25°.

In benzene.

f_2.	$\varepsilon_{25°}$.	$d^{25°}_{4°}$.	P_{12}.	P_2.
0·00000	2·2727	0·8736	26·612	—
0·01534	2·6224	0·8798	31·412	339·6
0·01688	2·6559	0·8805	31·832	335·9
0·02273	2·7894	0·8826	33·471	327·9
0·02910	2·9356	0·8849	35·170	320·7
0·03501	3·0717	0·8872	36·660	313·6

${}_{\infty}P_2 = 353{\cdot}8$; ${}_{\mathrm{E}}P_2 = 32{\cdot}6$; $P_{\mathrm{A+O}} = 321{\cdot}2$; $\mu = 3{\cdot}94$.*

In decalin.

f_2.	$\varepsilon_{25°}$.	$d^{25°}_{4°}$.	P_{12}.	P_2.
0·00000	2·1624	0·8809	43·793	—
0·01269	2·3158	0·8834	47·610	344·6
0·02150	2·4240	0·8851	50·119	338·0
0·02588	2·4790	0·8859	51·344	335·6
0·02618	2·4832	0·8860	51·434	335·6

${}_{\infty}P_2 = 352{\cdot}9$; ${}_{\mathrm{E}}P_2 = 32{\cdot}6$; $P_{\mathrm{A+O}} = 320{\cdot}3$; $\mu = 3{\cdot}93$.

* In Debye units (e.s.u. × 10^{-18}) here and throughout.

In carbon tetrachloride.

0·00000	2·2277	1·5848	28·186	—
0·01845	2·6031	1·5775	33·836	334·4
0·02444	2·7283	1·5751	35·522	328·5
0·03403	2·9307	1·5711	38·078	318·9

${}_{\infty}P_2 = 353{\cdot}1$; ${}_{\mathrm{E}}P_2 = 32{\cdot}6$; $P_{\mathrm{A+O}} = 320{\cdot}5$; $\mu = 3{\cdot}93$.

In n-*hexane.*

0·00000	1·8870	0·6615	29·705	—
0·01465	2·0896	0·6681	34·555	360·8
0·02819	2·2816	0·6740	38·704	349·0
0·04649	2·5508	0·6820	43·884	334·7

${}_{\infty}P_2 = 372{\cdot}5$; ${}_{\mathrm{E}}P_2 = 32{\cdot}6$; $P_{\mathrm{A+O}} = 339{\cdot}9$; $\mu = 4{\cdot}05$.

In cyclo*hexane.*

0·00000	2·0160	0·7739	27·493	—
0·02574	2·4563	0·7837	35·483	338·0
0·03229	2·5728	0·7860	37·349	332·7
0·03730	2·6608	0·7880	38·683	327·6
0·03938	2·6990	0·7890	39·240	325·8

$_{\infty}P_2$ = 360·0; $_{E}P_2$ = 32·6; P_{A+O} = 327·4; μ = 3·97.

In carbon disulphide.

0·00000	2·6328	1·2558	21·363	—
0·00769	2·8857	1·2546	23·529	303·1
0·01449	3·1105	1·2536	25·301	293·0
0·01846	3·2437	1·2530	26·290	288·2
0.02553	3·4830	1·2520	27·966	280·0

$_{\infty}P_2$ = 310·0; $_{E}P_2$ = 32·6; P_{A+O} = 277·4; μ = 3·66.

In chloroform.

0·00000	4·7219	1·4797	44·673	—
0·01620	5·2870	1·4747	47·648	228·4
0·02413	5·5598	1·4724	48·940	221·5
0·02875	5·7205	1·4711	49·661	218·2

$_{\infty}P_2$ = 241·2; $_{E}P_2$ = 32·6; P_{A+O} = 208·6; μ = 3·17.

DISCUSSION OF RESULTS.

The results are collected in Table I, ε being the dielectric constant of the solvent; $_{\infty}P_2$ falls with increasing dielectric constant of the solvent, and if it is plotted against 1/ε a good straight line results, as shown in Fig. 1. The points for *n*-hexane, *cyclo*hexane, carbon disulphide, and chloroform do not deviate from the line by more than 0·5 c.c., but those for benzene, carbon tetrachloride, and decalin (whose dielectric constants are close together) deviate by 18, 13, and 8 c.c. respectively. A hyperbolic relation may thus exist between polarisation and dielectric constant. Müller's results are also included in Fig. 1, but since they were made at 20° they are corrected to 25°.

TABLE I.

ε.	1/ε.	$_{\infty}P_2$.	μ.	ε.	1/ε.	$_{\infty}P_2$.	μ.
1·887	0·5299	372·5	4·05	2·273	0·4399	353·8	3·94
2·016	0·4960	360·0	3·97	2·633	0·3798	310·0	3·66
2·162	0·4625	352·9	3·93	4·722	0·2118	241·2	3·17
2·228	0·4488	353·1	3·93				

FIG. 1.

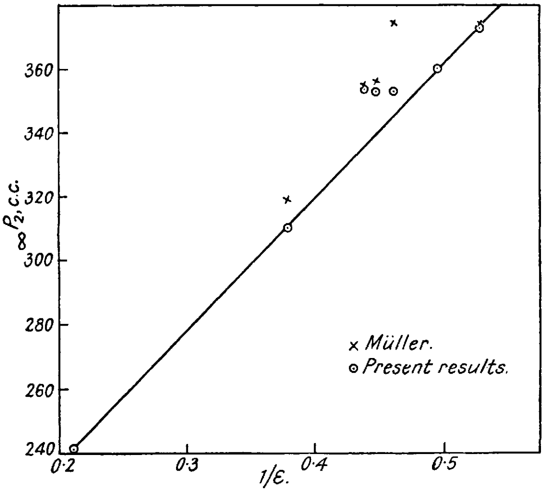
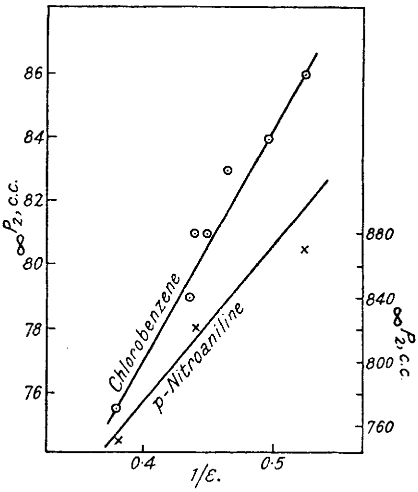


FIG. 2.



If now the line is extrapolated to ε = 1, a value of 570 c.c. is obtained, corresponding to an electric moment of 5·07. No value for nitrobenzene vapour is available, but it is extremely unlikely that such a high value would be obtained by application of the Debye equation and the temperature method.

The recent work of Fairbrother (*loc. cit.*) shows the same peculiarity. In this case the exact form of the relation between $_{\infty}P_2$ and dielectric constant cannot be derived, but since the moment even in benzene is larger than Zahn's value for the vapour, extrapolation to ε = 1 must give a moment 0·2—0·3 unit greater than the measured value for the gas, *viz.*, 1·03 (Zahn, *Physical Rev.*, 1924, **4**, 400). The fact that the moment (1·02) found in ethyl bromide coincides with the gas value is fortuitous. If the measurements had been made in chloroform, for example, a moment of about 1·1 would no doubt result. This is probably recognised by Fairbrother, although not stated in his paper.

The ${}_{\infty}P_2$–$1/\varepsilon$ relation tentatively proposed is illustrated in Fig. 2, also for the substances chlorobenzene and *p*-nitroaniline studied by Müller (*loc. cit.*; and *Physikal. Z.*, 1933, **34**, 689) at 20°. This worker has put forward the empirical equation $\mu_S/\mu_V = 1 - K(\varepsilon_S - 1)^2$, where μ_S is the moment in any solvent S, μ_V that of the vapour, and $K = 0{\cdot}038 \pm 0{\cdot}002$. Nitrobenzene has not been studied in the gas phase, but if μ_V is calculated from the results here communicated, values of 4·13—4·20 are obtained in the non-polar solvents and 6·69 in chloroform. However, an empirical rule can also be devised to hold in all the solvents studied. This is $\mu_S = 4{\cdot}30 - 0{\cdot}311\ (\varepsilon_S - 1)$. Table II gives the observed and calculated moments according to the above rule. The results make it quite clear that the dilute solution method does not, in general, measure the absolute electric moment of a polar molecule, but merely gives a qualitative indication of its true value. Whether the absolute value can be determined from a series of solution measurements is as yet uncertain.

TABLE II.

Solvent.	μ, obs.	μ, calc.
n-Hexane	4·05	4·02
*cyclo*Hexane	3·97	3·98
Decalin	3·93	3·94
Carbon tetrachloride	3·93	3·92
Benzene	3·93	3·92
Carbon disulphide	3·66	3·79
Chloroform	3·17	3·14

The diminution of what we shall call the apparent electric moment with increasing dielectric constant of the solvent will now be considered. The effective (local) field to which a molecule is subjected when a macroscopic field E is applied can be shown, on certain assumptions, to be $e_{\text{loc.}} = E + 4\pi I/3$ (where I is the electrodynamic polarisation vector), this being the usual Clausius–Mosotti formula. When this is applied to solutions, the solvent is generally assumed to influence the local field only as represented by addition of another term of the same type, the total local field now being

$$e_{\text{loc.}} = E + 4\pi I_1/3 + 4\pi I_2/3.$$

The Debye theory, assuming that the polarisation of the solvent is proportional to its concentration, then gives for the total polarisation of the mixture (with the usual notation):

$$P_{12} = P_1 f_1 + P_2 f_2 = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{f_1 M_1 + f_2 M_2}{d}$$

and

$${}_{\infty}P_2 = (4\pi N/3)(\alpha_0 + \mu^2/3kT).$$

Müller (*loc. cit.*) now considers that at molecular distances from the dipoles, in their intense electrical fields, electrical saturation is set up in the neighbouring solvent molecules. The orientation produced by the small applied field is thus less than in the pure solvent, and P_1 should be taken as a smaller value rather than as the value for the pure solvent. This explanation is based on Debye and Sack's interpretation of dielectric phenomena in electrolyte solutions. The decrease in the dielectric constant of salt solutions is explained by the appearance of the saturation effect in the strong electrical field of the ion. Müller on analogous lines has deduced a formula giving the fractional change in P_1 in terms of the reciprocal of the square of the dielectric constant of the solvent and some constants. This explanation may be on the right lines but one point must be noted. The experimental evidence for the saturation effect in electrolyte solutions is very conflicting owing to the difficulty of measuring the dielectric constants of conducting solutions. Experimental work indicates that sometimes dissolved ions raise the dielectric constant. Now, any explanation of the phenomenon must also include the relation between ${}_{\infty}P_2$ and $1/\varepsilon$, which holds also in the polar solvent chloroform. The contribution of such solvents to the local field in the Clausius–Mosotti equation should not be given by $4\pi I_1/3$.

Apparently, however, there is no distinction between non-polar and polar solvents, as regards the measurements of polarisations.

It is easy to deduce a formula giving an increase of apparent moment with decreasing dielectric constant, but further experimental results are being obtained before this is discussed.

SUMMARY.

A systematic investigation of the molecular electrical polarisations of nitrobenzene in various solvents at 25° has been made. The dilute solution method has been shown not to give, in general, the dipole moment of a molecule.

A relation between polarisation and reciprocal of dielectric constant of solvent has been found. Apparently there is no difference between non-polar and polar solvents as regards this relation.

[*Note, added March* 10*th*, 1934.] It was of interest to find out whether the polarisations of the pure substances, nitrobenzene and chlorobenzene, lay on their corresponding ${}_{\infty}P_2$–$1/\varepsilon$ lines. Calculation from the work of Sugden (J., 1933, 768) indicates that chlorobenzene obeys the rule right up to the pure liquid, but nitrobenzene does not. Some preliminary work by the author also indicates that ${}_{\infty}P_2$ for chlorobenzene in chloroform falls closely on the line.

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