221. *Solvent Effect in Dielectric Polarisation. Parts I and II.*

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PART I. THE POLARISATIONS OF NITROBENZENE AND CHLOROBENZENE IN CERTAIN ETHERS.

SINCE the publication (*Physikal. Z.*, 1933, **34**, 689; 1934, **35**, 346; *Trans. Faraday Soc.*, 1934, **30**, 729) of Müller's investigations of the influence of the dielectric constant of the solvent on the polarisation and apparent moment of solute molecules, much attention has been given to this phenomenon. Work has been, for the most part, directed towards the formulation of an expression which would make possible the calculation of the moment in the vapour state from measurements in one or more solvents. The present position is reviewed in detail by Glasstone (*Ann. Reports*, 1936, **33**, 117 *et seq.*). Empirical formulæ have been proposed by Müller (*loc. cit.*), Sugden (*Nature*, 1934, **133**, 413; *Trans. Faraday Soc.*, 1934, **30**, 720), and Jenkins (J., 1934, 480); theoretical relationships have been advanced by Weigle (*Helv. Physica Acta*, 1933, **6**, 68), Rau (*Proc. Indian Acad. Sci.*, 1935, *A*, **1**, 498), Le Fèvre (*Nature*, 1935, **136**, 181; J., 1935, 1747), Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171), and Higasi (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 284). The equations derived by Rau and Le Fèvre are based on Raman and Krishnan's theory (*Proc. Roy. Soc.*, 1928, *A*, **117**, 589) of the relationship between the polarisation and the dielectric constant of a pure substance in the liquid state. Sugden's empirical equation bears a resemblance to the Raman and Krishnan equation, as was first pointed out by Goss (J., 1933, 1341; 1934, 696), but its validity from the standpoint of the experimental evidence was questioned by Jenkins and Sutton (J., 1935, 609), and more recently the assumptions involved in Raman and Krishnan's treatment of the subject have been adversely criticised by Mueller (*Physical Rev.*, 1936, **50**, 547) and Jenkins and Bauer (*J. Amer. Chem. Soc.*, 1936, **58**, 2435).

The present work was undertaken in order to test the applicability of some of these equations over a wider range of dielectric constant than is afforded by the non-polar solvents commonly used in such work, which have only a limited range varying from about 1·9 for hexane to about 2·7 for carbon disulphide (depending on the temperature at which the measurements are made). Polar solvents have higher dielectric constants and some have been used (for references see *Ann. Reports*, 1936, **33**, 133), but such solvents are not all suitable for this work, since in calculating the polarisation of the solute that of the solvent is assumed to be independent of its concentration. If this condition is not satisfied, estimation of the polarisation of the solute at infinite dilution, whether by graphical extrapolation or by calculation, seems of questionable validity. Higasi (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, **24**, 57) has used ethyl ether as a solvent: its polarisation in solution in benzene is remarkably constant except in very dilute solutions, in which there is a slight increase; its disadvantages are patent. In the present work the use of the higher aliphatic ethers has been investigated. The polarisations of di*iso*propyl, di-*n*-butyl, and diamyl ethers have been measured in benzene solutions. The values, although not quite constant, vary only very slightly in the range of concentrated solutions, the range corresponding to the dilute solution range when the ethers are used as solvents. The dielectric constants decrease as one goes up the series, and are of the orders 4·0, 3·1, and 2·8 respectively, providing a useful extension to the range of solvents previously used in work of this kind. The polarisations of nitrobenzene and of chlorobenzene have been measured by using these ethers as solvents. The extrapolated values at infinite dilution are collected below.

	Total polarisation.	
Solvent.	Nitrobenzene.	Chlorobenzene.
*iso*Propyl ether	293	68·8
n-Butyl ether	341	79·3
Amyl ether	350	81

Nitrobenzene, $P_E + P_A = 36{\cdot}2$; chlorobenzene, $P_E + P_A = 34{\cdot}9$ (Groves and Sugden, J., 1934, 1094).

Table I collates the values for ${}_{\infty}P_O$ derived from these measurements with the values found by Jenkins in various solvents and with the value for the vapour calculated from the results of Groves and Sugden (*loc. cit.*); it also includes a measurement of ${}_{\infty}P_O$ for nitrobenzene in carbon disulphide made in the course of the present work.

TABLE I.

Nitrobenzene at 25°.

Solvent.	${}_{\infty}P_O$.	$\sqrt{{}_{\infty}P_O}$.	$\epsilon_{solv.}$.	$1/\epsilon$.	$(\epsilon - 1)^2$.
Hexane	336·3	18·34	1·8870	0·530	0·787
*cyclo*Hexane	323·8	17·99	2·0160	0·496	1·032
Decalin	316·7	17·80	2·1624	0·4625	1·350
Carbon tetrachloride	316·9	17·80	2·2277	0·4488	1·508
Benzene	317·6	17·82	2·2725	0·4399	1·620
Carbon disulphide *	286·4	16·92	2·6330	0·3798	2·666
Carbon disulphide †	273·8	16·55	2·6328	0·3798	2·664
Amyl ether	313·8	17·71	2·7980	0·3596	3·235
n-Butyl ether	304·8	17·46	3·0817	0·3249	4·335
*iso*Propyl ether	256·8	16·03	4·0370	0·2365	9·222
Chloroform	205·0	14·32	4·722	0·2118	13·85
(Vapour)	367·0	19·3	1·000	1·000	0

* Present work. † Jenkins.

The data of Table I are plotted in Fig. 1. If the values of ${}_{\infty}P_O$ are plotted against the dielectric constant of the solvent, a smooth curve can be drawn through the values in the ethers, in chloroform, in hexane, and for the vapour state. The values in carbon disulphide fall far below this curve, and the values found in the non-polar solvents benzene, *cyclo*hexane, decalin, and carbon tetrachloride fall about 10 c.c. below it. If, now, following Müller's empirical rule (*loc. cit.*)

$$P_O\text{, soln.} = P_O\text{, gas } [1 - \text{constant } (\varepsilon - 1)^2]$$

we plot the values of P_O in solution against $(\varepsilon - 1)^2$, a straight line is given by the points which formerly fell on the curve, and again the values in the same five solvents fall below the line, the values in carbon disulphide being very much below it. This straight line at $(\varepsilon - 1)^2 = 0$ gives $P_O = 345$ c.c. The gas value calculated for 25° is 367 c.c. The values have also been plotted according to the rules of Jenkins (*loc. cit.*: ${}_{\infty}P_O$ against $1/\varepsilon$) and Frank (*loc. cit.*: $\sqrt{{}_{\infty}P_O}$ against $1/\varepsilon$). In each case the values in the non-polar solvents (except carbon disulphide) give an approximately linear graph which the values in the polar solvents carry into a smooth curve. The exceptional position of carbon disulphide must again be noted; it behaves, in fact, as though it had a very much higher dielectric constant. This appears to be its general behaviour with substances whose molecules have a radical on the dipole axis.

In each of these two graphs, extrapolation to $1/\varepsilon = 1$ can have little real significance, since the highest value available for $1/\varepsilon$ on the straight-line portion is only 0·530 and the lowest value about 0·36.

By using Higasi's formula (*loc. cit.*, 1936) calculations have been made of the moment of nitrobenzene in solutions in *iso*propyl, *n*-butyl, and amyl ethers. The equations are

$$\mu_{soln.} = \mu_{gas} + \Sigma\mu_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\Sigma\mu_i = 4\pi n\alpha\mu A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $4\pi n\alpha = 3(\varepsilon - 1)/(\varepsilon + 2)$ for the solvent, μ is the value of the moment of the solute in the vapour state, and A is given by the expression

$$A = -\frac{1}{K^2 - 1}\left\{1 - \frac{K}{\sqrt{K^2 - 1}}\log\left(K + \sqrt{K^2 - 1}\right)\right\} - \tfrac{1}{3}$$

in which K is a parameter depending on the shape of the solute molecule and is evaluated from the Kerr constant.

FIG. 1.

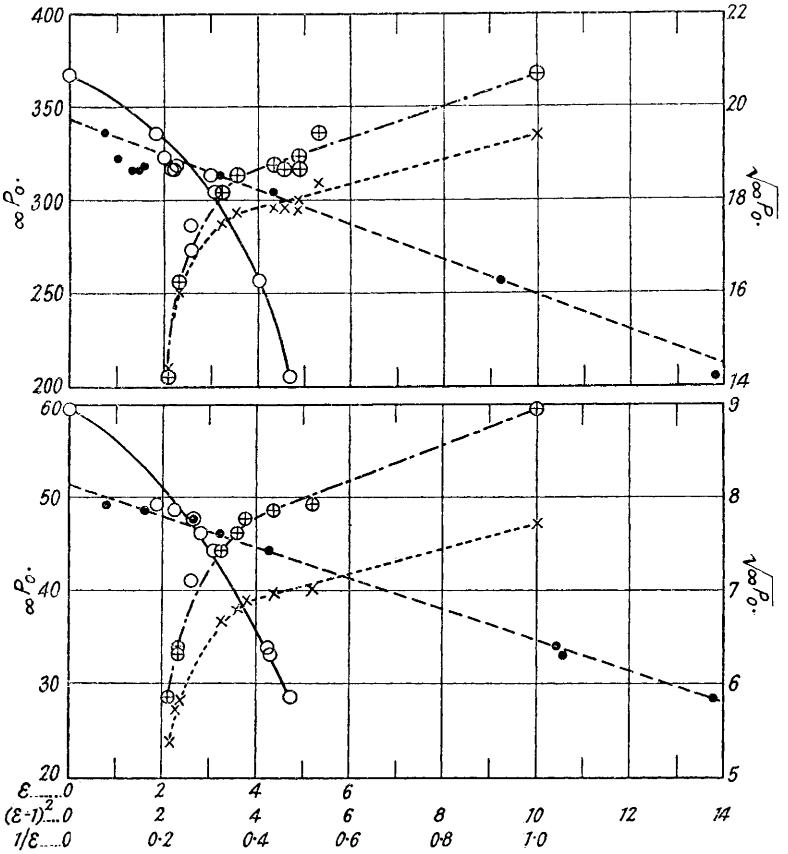


FIG. 2.

○——○——○ $_{\infty}P_0$ against ε solvent.
●– – –●– – –● $_{\infty}P_0$ " $(\varepsilon-1)^2$ "
⊕—·—⊕—·—⊕ $_{\infty}P_0$ " $1/\varepsilon$ "
×------×------× $\sqrt{_{\infty}P_0}$ " $1/\varepsilon$ "

For nitrobenzene, $K = 1{\cdot}69$, whence A is calculated to be $-0{\cdot}128$, and the moment of nitrobenzene in the vapour state being taken as 4·23 (Groves and Sugden, *loc. cit.*), the following values are found :

Solvent.	$4\pi n\alpha$.	$\Sigma\mu_i$.	$\mu_{\text{calc.}}$.	$\mu_{\text{obs.}}$.
*iso*Propyl ether	1·509	−0·82	3·41	3·51
n-Butyl ether	1·229	−0·66	3·57	3·83
Amyl ether	1·125	−0·61	3·62	3·88

The values of P_0 found for chlorobenzene in these ethers and in carbon disulphide are compared in Table II with results obtained in various solvents at the same temperature by other workers. Fig. 2 expresses these data in graphical form.

TABLE II.

Chlorobenzene at 25°.

Solvent.	$_{\infty}P_O$.	$\sqrt{_{\infty}P_O}$.	$\epsilon_{solv.}$.	$1/\epsilon$.	$(\epsilon - 1)^2$.
Hexane [1]	49·1	7·007	1·904	0·525	0·817
Benzene [2]	48·7	6·98	2·273	0·440	1·620
Carbon disulphide [1]	47·6	6·90	2·633	0·380	2·664
Carbon disulphide	40·9	6·39	2·633	0·380	2·664
Amyl ether	46·1	6·79	2·798	0·360	3·235
Butyl ether	44·4	6·66	3·087	0·325	4·335
*iso*Propyl ether	33·9	5·82	4·232	0·236	10·45
Ethyl ether [3]	33·1	5·75	4·25	0·235	10·56
Chloroform [4]	28·7	5·36	4·722	0·212	13·85

[1] Williams and Ogg, *J. Amer. Chem. Soc.*, 1928, **50**, 94. [2] Smyth, Morgan, and Boyce, *ibid.*, p. 1536. [3] Higasi, *loc. cit.*, 1934. [4] Jenkins, *Trans. Faraday Soc.*, 1934 (Appendix).

If $_{\infty}P_O$ is plotted against ε for the solvent, a smooth curve is obtained from which no point deviates by more than 1·5 c.c. except the present author's value in carbon disulphide solution. Williams and Ogg's value appears to be too high, as does their value for nitrobenzene in carbon disulphide given in the same paper.

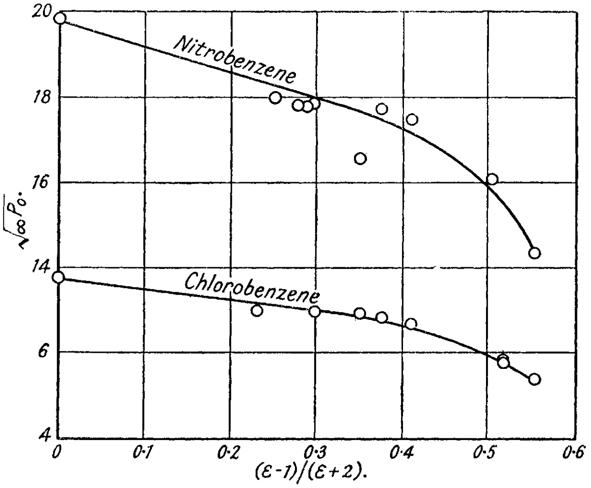
If $_{\infty}P_O$ is plotted against $(\varepsilon - 1)^2$ (Müller's relationship), a very good straight line is obtained, no point deviating by more than 1·0 c.c., save the value in carbon disulphide. This straight line at $(\varepsilon - 1)^2 = 0$ gives $P_O = 51{\cdot}4$, as compared with the value 59·5 for the vapour at 25° calculated from Groves and Sugden's data (*loc. cit.*). Graphed according to the rules of Jenkins and of Frank, the same types of curves are obtained as in the case of nitrobenzene.

Applying Higasi's equations and taking μ vap. = 1·69 (Groves and Sugden, *loc. cit.*), we obtain the following values: $K = 1{\cdot}53$, whence $A = -0{\cdot}105$.

Solvent.	$4\pi n\alpha$.	$\Sigma\mu_i$.	$\mu_{calc.}$.	$\mu_{obs.}$.
*iso*Propyl ether	1·556	−0·276	1·41	1·28
n-Butyl ether	1·229	−0·218	1·47	1·46
Amyl ether	1·125	−0·199	1·49	1·56

It is evident from these collected data on both nitrobenzene and chlorobenzene that Jenkins's rule ($_{\infty}P_O$ linear with 1/ε) is unsound in that it certainly does not cover the case of polar solvents as was originally claimed. Frank's rule ($\sqrt{_{\infty}P_O}$ linear with 1/ε) also fails to cover the case of polar solvents; further, both are unsatisfactory for non-polar

FIG. 3.



solvents in that estimation of the gas value from the solution values involves a most uncertain extrapolation.

Higasi's equation may be re-written

$$\mu_{\text{soln}} = \mu_{\text{gas}} (1 - 4\pi n \alpha A)$$

and since $4\pi n\alpha$ is proportional to $(\varepsilon - 1)/(\varepsilon + 2)$, we may represent it graphically by plotting ${}_{\infty}P_{\text{O}}$ against $(\varepsilon - 1)/(\varepsilon + 2)$. This gives a curve, not a straight line (cf. Fig. 3).

On the other hand, the linearity of ${}_{\infty}P_{\text{O}}$ with $(\varepsilon - 1)^2$ (Müller's relationship) is most striking, even though the deduced values of P_{O} for the vapour are lower than the experimental values. Such low values from Müller's equation have already been noted by Cowley and Partington (J., 1936, 1184; this vol., p. 130).

EXPERIMENTAL.

Apparatus.—The resonance method was used, the oscillator being the dynatron circuit used by Sugden (J., 1933, 768). The measuring circuit differed from his in that, since no precision variable condenser was available, the arrangement of condensers described by Sayce and Briscoe (J., 1925, **127**, 315) was adopted. The small, single-plate, variable condenser was controlled by a brass worm engaging a fibre worm wheel attached to the condenser spindle. All the condensers were carefully shielded. The inductances of the measuring circuit were wound on formers built up of " Keramot " strips supported on special three-pin bases which plugged into the apparatus. Irregularities were at first experienced when ebonite was used as the insulating material in the measuring circuit, but the substitution of " Keramot," which has greatly superior surface properties, eliminated these satisfactorily. The dielectric cells were of the Sayce–Briscoe type.

Densities were measured in a quartz pyknometer. To test the accuracy of the apparatus, a series of measurements was made of the polarisation of nitrobenzene in benzene at 25°. This gave $P_2 = 355$ c.c., whereas Jenkins found 353·8 (*Nature*, 1934, **133**, 106). It is considered that the error in values of P_2 is not greater than 0·5%.

Materials.—Di*iso*propyl, di-*n*-butyl, and diamyl ethers were purchased. They were refluxed over sodium for several days, dried for 2 or 3 days over phosphoric oxide, and finally distilled from sodium through a long column in a current of dry nitrogen. It is difficult to ensure that these products are free from isomers : different specimens of the same ether were obtained with different physical constants, though test showed that peroxides were absent; *e.g.*, the amyl ether is probably a mixture of the active and the *iso*-ether. This variability does not affect the validity of work carried out with these solvents since we are concerned only with the effect of the dielectric constant of the solvent on the polarisation of the solute. The following physical constants are recorded : Di*iso*propyl ether, b. p. 67·2—67·4°/734·5 mm., $d_{4^\circ}^{25^\circ}$ 0·72002, ε_{25° 4·0370, $n_{\text{D}}^{25^\circ}$ 1·36658; a second specimen, b. p. 68·5—68·9°/770 mm., had $d_{4^\circ}^{25^\circ}$ 0·72185, ε_{25° 4·2321; di-*n*-butyl ether, b. p. 138·5—139·5°/754 mm., $d_{4^\circ}^{25^\circ}$ 0·76420, ε_{25° 3·0817, $n_{\text{D}}^{25^\circ}$ 1·39732; diamyl ether, b. p. 168—169°/755 mm., $d_{4^\circ}^{25^\circ}$ 0·77149, ε_{25° 2·7880, $n_{\text{D}}^{25^\circ}$ 1·40590, $\alpha_{5461}^{20^\circ}$ (2 dm.) 1·0°; a second specimen, b. p. 169—170°/770 mm., had $d_{4^\circ}^{25^\circ}$ 0·77165, ε_{25° 2·8220, $n_{\text{D}}^{25^\circ}$ 1·40646.

Benzene. Benzene for use in calibrating the dielectric cells was prepared from B.D.H. "extra pure" liquid by three fractional crystallisations, followed by drying over phosphoric oxide and distillation therefrom through a Widmer column. Its dielectric constant was assumed to be 2·2725 at 25°. The benzene used as a solvent in measuring the polarisations of the ethers was prepared from commercial " crystallisable " benzene by several hours' shaking with mercury, filtration, repeated shaking with concentrated sulphuric acid till no thiophen reaction was given, washing with sodium carbonate solution, then with water, and several days' drying over phosphoric oxide and distillation through a long column. The fraction, b. p. 80°, was collected. Its dielectric constant was lower than that of pure benzene and varied slightly from specimen to specimen, probably on account of the presence of aliphatic hydrocarbons.

Nitrobenzene. Nitrobenzene, prepared according to Masson (*Nature*, 1931, **128**, 726), had m. p. 5·65°.

Chlorobenzene. A commercial specimen was washed with dilute caustic soda solution, then with water, dried over calcium chloride and fractionated through a column; it had b. p. 131·4—131·6°/748 mm., $d_{4^\circ}^{25^\circ}$ 1·1016, $n_{\text{D}}^{25^\circ}$ 1·5222.

Carbon disulphide. Carbon disulphide " AnalaR " was shaken with mercury for several days, filtered, and fractionally distilled from iron turnings through a long column. The middle fraction, b. p. 45·9°/750 mm., was taken; it had $d_{4^\circ}^{25^\circ}$ 1·2566, ε_{25° 2·6330.

Results.—In the following tables the symbols have the usual significance.

iso*Propyl ether in benzene.*

f_2.	$d_{4°}^{25°}$.	$\epsilon_{25°}$.	P_2.
0·0000	0·87153	2·2680	—
0·04153	0·86253	2·3512	71·25
0·08560	0·85385	2·4390	71·10
0·12468	0·84615	2·5176	71·31
0·1255	0·84595	2·5185	71·22
0·17733	0·83504	2·6228	71·72
1·0000	0·72002	4·0370	71·34

n-*Butyl ether in benzene.*

f_2.	$d_{4°}^{25°}$.	$\epsilon_{25°}$.	P_2.
0·0000	0·87165	2·2705	—
0·014462	0·86777	2·2878	73·4
0·018621	0·86667	2·2928	73·5
0·025644	0·86483	2·3014	72·9
0·041543	0·86090	2·3206	72·1
0·046219	0·85970	2·3263	72·1
0·059866	0·85900	2·3418	71·4
0·12165	0·84684	2·4197	71·1
0·2900	0·82176	2·5962	70·6
0·57566	0·79199	2·8212	69·85
0·7364	0·78024	2·9315	69·76
1·0000	0·76420	3·0817	69·68

Amyl ether in benzene.

f_2.	$d_{4°}^{25°}$.	$\epsilon_{25°}$.	P_2.
0·0000	0·87154	2·2668	—
0·016642	0·86750	2·2845	77·4
0·026735	0·86515	2·2964	78·3
0·03434	0·86316	2·3049	78·6
0·051766	0·85953	2·3228	78·3
0·079138	0·85397	2·3512	78·4
0·13453	0·84363	2·4042	78·5
0·24410	0·82709	2·4902	78·10
0·41682	0·80762	2·5919	77·60
0·64046	0·79015	2·6957	77·4
0·73526	0·78447	2·7315	77·3
1·0000	0·77149	2·7980	76·83

Nitrobenzene in iso*propyl ether.*

0·0000	0·72002	4·0370	—
0·018657	0·72775	4·4375	278·6
0·033633	0·73388	4·7675	269·4
0·046452	0·73901	5·0430	259·3
0·066485	0·74741	5·4979	247·8
0·11592	0·76801	6·5633	218·8
0·167804	0·78929	7·670	196·3

$_{\infty}P_2 = 293.$

Nitrobenzene in n-*butyl ether.*

0·0000	0·76420	3·0817	—
0·00706	0·76645	3·1900	331·3
0·01274	0·76845	3·2773	326·5
0·017803	0·76990	3·3518	319·7
0·021237	0·77084	3·4040	317·3
0·032106	0·77397	3·5730	310·6

$_{\infty}P_2 = 341.$

Nitrobenzene in amyl ether.

0·0000	0·77149	2·7980	—
0·011968	0·77397	2·9368	338·7
0·01996	0·77610	3·0315	333·8
0·028604	0·77830	3·1329	324·4
0·03801	0·78048	3·2407	315·9
0·06145	0·78581	3·5280	300·7

$_{\infty}P_2 = 350.$

Chlorobenzene in iso*propyl ether.*

0·0000	0·72185	4·2321	—
0·01785	0·72755	4·2643	68·1
0·036527	0·73351	4·2948	67·2
0·051519	0·73820	4·3192	67·1
0·07037	0·74449	4·3517	66·7
0·084398	0·74880	4·3768	67·07
0·098722	0·75360	4·3995	66·66
0·17718	0·77882	4·5210	66·07

$_{\infty}P_2 = 68·8.$

Chlorobenzene in n-*butyl ether.*

0·0000	0·76420	3·0817	—
0·022484	0·76916	3·1265	77·0
0·04385	0·77400	3·1685	78·0
0·053446	0·77633	3·1880	77·7
0·081235	0·78242	3·2435	77·4
0·12493	0·79251	3·3301	76·2
0·17659	0·80481	3·4390	75·5

$_{\infty}P_2 = 79·3.$

Chlorobenzene in amyl ether.

0·0000	0·77149	2·7980	—
0·010784	0·77340	2·8157	80·5
0·021883	0·77565	2·8354	80·8
0·034236	0·77798	2·8559	80·0
0·048486	0·78066	2·8812	80·2
0·10081	0·79054	2·9700	78·5
0·17528	0·80480	3·0998	76·2
0·26470	0·82504	3·2822	74·9

$_{\infty}P_2 = 81.$

Nitrobenzene in carbon disulphide.

0·0000	1·2566	2·6330	—
0·004070	1·2560	2·7722	319·1
0·007494	1·2552	2·8862	310·6
0·008696	1·2550	2·9290	310·3
0·016248	1·2539	3·1869	298·4
0·024270	1·2529	3·4605	286·7
0·02522	1·2525	3·4990	286·8
0·037338	1·2512	3·9081	270·3

$_{\infty}P_2 = 322·6.$

Chlorobenzene in carbon disulphide.

0·0000	1·2566	2·6330	—
0·007829	1·2543	2·6692	75·4
0·014479	1·2523	2·6984	74·7
0·03060	1·2477	2·7694	74·1
0·048527	1·2424	2·8507	74·07
0·063287	1·2385	2·9176	73·78

$_{\infty}P_2 = 75·8.$

PART II. NOTE ON POSITIVE SOLVENT EFFECT OF BUTYL AND AMYL ETHERS.

IT is now generally recognised that, although most substances show a lower polarisation in solution than in the gaseous state, yet there exist some which exhibit an opposite behaviour. These phenomena have been related to the Kerr constant by Higasi (*Bull. Inst. Phys. Chem. Res. Tokyo*, 1935, *A*, **152**, 171; *loc. cit.*, 1936) and Rau (*loc. cit.*). It is predicted that, according as the substance has a positive or a negative value of the Kerr constant, the moment in solution will be respectively lower or higher than that in the gaseous state (" negative " or " positive " solvent effect). Similar conclusions regarding the relation between the sign of Kerr constant and that of the solvent effect are reached by Le Fèvre (*locc. cit.*).

Ethers have negative values of Kerr constant, and for ethyl ether a " positive " solvent effect has been observed (Higasi, *loc. cit.*). For butyl and amyl ethers no measurements of the polarisation in the gaseous state are available. If, however, these substances exhibit a " positive " solvent effect the polarisation in solution should decrease as the dielectric constant of the solvent decreases. It is found that for each ether the polarisation in hexane is lower than in benzene at the same temperature and also lower than that of the liquid ether. The values are:

	Pure ether.	In benzene.	In hexane.
	P.	P_2.	P_2.
n-Butyl ether	69·68	74·5	68·6
Amyl ether	77·45	78·6	74·5

The effect observed is smaller for amyl than for butyl ether. This is probably to be expected, since the recorded Kerr constants of the ethers as vapours decrease in the order dimethyl > diethyl > di-*n*-propyl. No data are available for the Kerr constants of butyl and amyl ethers.

The hexane used was *n*-hexane "free from aromatic hydrocarbons" freshly distilled from phosphoric oxide; b. p. 68·7—68·9°/745 mm., $d_{4^\circ}^{25^\circ}$ 0·66662, ε_{25° 1·8863.

The measurements are as follows:

Butyl ether in n-*hexane.*

f_2.	$d_{4^\circ}^{25^\circ}$.	ϵ_{25°.	P_2.
0·0000	0·66662	1·8863	—
0·020544	0·66916	1·9102	68·8
0·04440	0·67267	1·9390	68·82
0·10019	0·67939	2·0063	69·41
0·19716	0·69082	2·1215	69·32
0·38624	0·71163	2·3480	69·44
0·63757	0·73559	2·6528	69·65
0·84250	0·75290	2·8946	69·61
1·0000	0·76420	3·0817	69·68

${}_{\infty}P_2 = 68{\cdot}6$.

Amyl ether in n-*hexane.*

f_2.	$d_{4^\circ}^{25^\circ}$.	ϵ_{25°.	P_2.
0·0000	0·66662	1·8863	—
0·01989	0·66975	1·9076	74·7
0·038187	0·67271	1·9273	74·77
0·065344	0·67736	1·9582	75·34
0·091623	0·68148	1·9855	75·10
0·18150	0·69478	2·0863	76·25
0·32879	0·71300	2·2439	77·15
0·68072	0·74805	2·5698	77·37
0·79597	0·75733	2·6619	77·29
1·0000	0·77165	2·8220	77·45

${}_{\infty}P_2 = 74{\cdot}5$.

SUMMARY.

The polarisations of nitrobenzene and chlorobenzene in *iso*propyl, *n*-butyl, and amyl ethers are found to be consistent with the results obtained in other solvents, including chloroform.

The linear relationships proposed by Jenkins, Frank, and Higasi are found to be invalid for polar solvents.

The empirical relationship proposed by Müller is found to give a linear graph for polar and non-polar solvents, though extrapolation gives a value for the gaseous state which is too low.

Measurements of the polarisations of butyl and amyl ethers in benzene and in hexane show a decrease in polarisation with decreasing dielectric constant of solvent as has been predicted for substances with negative values of Kerr constant.

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