402. *The Magnitude of the Solvent Effect in Dipole-moment Measurements. Part I. The Polarisation of Carbon Tetrachloride Solutions.*

By F. R. Goss.

The dielectric polarisation of polar substances in solution is known to differ from the same polarisation measured in the vapour state by amounts which are described in general as "solvent effects." It is already known that these are connected with the electrical anisotropy of the solvent, the concentration, anisotropy, and degree of association of the solute, and any chemical reaction which may occur between solvent and solute.

It is now shown that for certain solutions of polar substances in the isotropic solvent, carbon tetrachloride, the variation in the partial molar polarisations (P_S), obtained by the method of intercepts from the polarisations (P_{12}) of the mixtures, can be expressed as a function of the dielectric constant ε in the form

$$P_S = P_{E+A} + Z(\varepsilon - 1)^4/(\varepsilon + 2)^4 + Y/\varepsilon$$

Here Y and Z are molar quantities whose ratios (Y/P_0 and Z/P_{E+A}) to the orientation and to the distortion polarisations respectively are, in the same way as $(P_\infty - P_{E+A})/P_0$, a measure of the modification of the magnitude of the polarisation by the anisotropy. These quantities are found to be related by the formula

$$(Y/P_0 - 1)/[\sqrt[4]{(Z + P_{E+A})/P_{E+A}} - 1] = 3{\cdot}25$$

by means of which the solvent effects due to anisotropy and change of concentration may readily be defined and calculated.

Values for the dipole moment obtained by means of these formulæ from suitable experimental data are in satisfactory agreement with those given by the vapour measurements.

FOLLOWING the successful interpretation (J., 1933, 1341) of the temperature variation of the polarisation of certain non-polar liquids in terms of dielectric anisotropy, an attempt was made (J., 1934, 696, 1467) to find a theoretical basis for Sugden's relation (*Nature*, 1934, **133**, 415)

$$P_2 = P_{E+A+O} + \alpha - P_O(\varepsilon - 1)/(\varepsilon + 2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for the dielectric polarisation P_2 of one component of a liquid mixture in terms of the total and the orientation polarisation, P_{E+A+O} and P_O, of the same substance in the state of vapour, and the dielectric constant of the mixture, the term α being obtained experimentally. This simple formula was found to require modification (cf. J., 1935, 502) when applied to mixtures of carbon tetrachloride and nitrobenzene [an example chosen both for the isotropic nature of the non-polar solvent (cf. J., 1935, 727) and for the wide range covered by the values of ε in this case]. It was found that a close approximation to the experimental data is given by the expression

$$P_2 = P_{E+A+O} - B\{(\varepsilon - 1)/(\varepsilon + 2) + (\varepsilon - 1)^2/(\varepsilon + 2)^2\} \quad . \quad . \quad . \quad (2)$$

Unfortunately (1) and (2) are not generally applicable to mixtures of other liquids which have been examined, and it is evident that agreement between such formulæ and the data must be largely fortuitous because the values of P_2 are calculated on the quite arbitrary assumption, due in the first place to Debye (Marx, "Handbuch der Radiologie," 1925, **6**, 630), that the polarisation P_1 of the other component is independent of the concentration c_2. This assumption admittedly leads to the correct value for the polarisation P_∞ of the solute at infinite dilution ($c_2 = 0$), although considerable uncertainty must necessarily be introduced into the extrapolation because of the arithmetical difficulty involved in employing the expression (3) at small values of c_2.

$$P_2 = (P_{12} - P_1)/c_2 + P_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

On the other hand, the values of P_2 given by formula (3) for finite values of c_2 will be wrong to the extent that Debye's assumption of the invariability of P_1 is in error.

Orr and Butler (*Nature*, 1932, **130**, 930) believe that the intercept method * gives the partial polarisations of the components of a mixture at all concentrations, and in this communication an attempt is made to interpret the intercepts (P_{S1} and P_{S2}) given by tangents to P_{12} curves at the axes where $c_2 = 0$ and 1 (see Fig. 1) in the expectation that they represent the partial polarisations more exactly than P_1 and P_2 obtained in the usually accepted manner.

As an example of the method, in Fig. 1 values of P_{12} for chlorobenzene (Table III) are plotted against c_2, and it will be seen that the tangent at the point where $c_2 = 0{\cdot}47942$, one of the experimental points, gives the intercepts of $P_{S1} = 33$ and $P_{S2} = 65$ as the partial polarisations of carbon tetrachloride and chlorobenzene respectively at this concentration, whereas by (3) the values are $P_1 = 28$ and $P_2 = 70$.

Now, it is undoubtedly true that, since the intercepts may be read with almost equal accuracy at all concentrations, P_∞, which is the intercept given by the tangent at the point where $c_2 = 0$, is obtainable more accurately and more readily than by extrapolation

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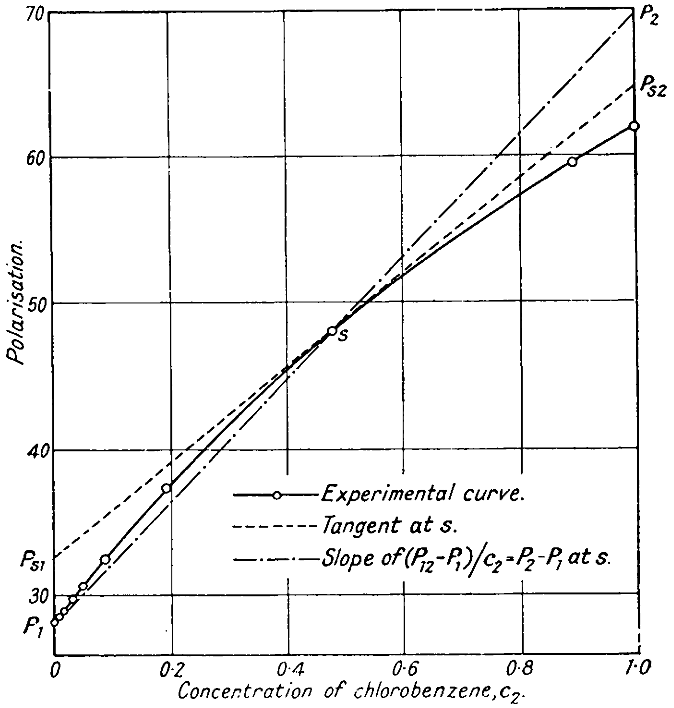
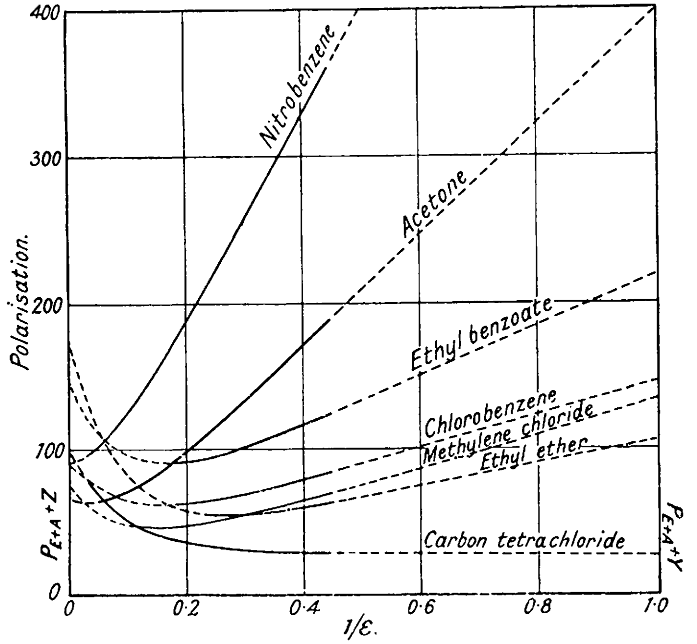
Fig. 1.



Polarisation of chlorobenzene and carbon tetrachloride at 20°.

Fig. 2.



Partial molar polarisations at 20° $P_S = P_{E+A} + Z(\epsilon - 1)^4/(\epsilon + 2)^4 + Y/\epsilon$ *extrapolated to* $\epsilon = 1$ *and* $\epsilon = \infty$.

of P_2. Further, it will be seen from the data given in Table I that the intercepts obtained from mixtures of carbon tetrachloride with several polar substances, each component being considered independently, can be expressed as a function of the dielectric constant :

$$P_S = P_{E+A} + Z(\varepsilon - 1)^4/(\varepsilon + 2)^4 + Y/\varepsilon \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The values of P_S given by (4), which are also given in Fig. 2, are seen to coincide with the actual intercepts except for minor deviations in the case of the higher concentrations of ethyl ether, nitrobenzene, and carbon tetrachloride; in the other four cases agreement is exact.

TABLE I.

$t = 20°$.

Nitrobenzene (Pal, *Phil. Mag.*, 1930, **10**, 265); $[R_L]_D = 32{\cdot}7$; $P_{E+A} = 34{\cdot}3$.

c_2.	P_{S_2}.	P_{S_1}.	P_{S_2} [calc. by (4)].
0·00000	365	28·0	365
0·00985	337	28·1	337
0·02101	311	28·6	310
0·03193	290	29·2	288
0·04686	264	30·4	263
0·07064	232	32·5	231
0·09586	205	35	205
0·1527	167	41	168
0·2098	143	47	144
0·3103	119	54	124
0·4039	109	59	112
0·5001	103	64	105
0·5917	99	68	102
0·7166	96	72	98
0·8046	95	75	97
0·8936	94·7	78	95
1·0000	94·5	80	94·5

Ethyl benzoate (see Table III); $[R_L]_D = 42{\cdot}6$; $P_{E+A} = 44{\cdot}7$.

c_2.	P_{S_2}.	P_{S_1}.	P_{S_2} [calc. by (4)].
0·00000	124	28·1	124
0·00645	123	28·1	123
0·01351	122	28·1	122
0·03413	119	28·2	119
0·05252	116	28·4	116
0·06868	114	28·5	114
0·10835	109	29	110
0·18000	103	30	104
0·41006	94	34	94
0·67061	91	38	91
1·00000	89·8	42	89·8

Methylene chloride (Morgan and Lowry, *J. Physical Chem.*, 1930, **34**, 2385); $[R_L]_D = 16{\cdot}3$; $P_{E+A} = 17{\cdot}1$.

c_2.	P_{S_2}.	P_{S_1}.	P_{S_2} [calc. by (4)].
0·00000	70	28·2	70
0·25000	57	30	57
1·00000	46·8	53	46·8

Chlorobenzene (see Table III); $[R_L]_D = 31{\cdot}2$; $P_{E+A} = 32{\cdot}8$.

c_2.	P_{S_2}.	P_{S_1}.	P_{S_2} [calc. by (4)].
0·00000	85	28·1	85
0·00806	84	28·1	84
0·01531	83	28·1	83
0·03142	82	28·2	82
0·04812	81	28·2	81
0·08478	79	28·2	79
0·18906	74	29	74
0·47942	65	33	66
0·89470	62	39	62
1·00000	61·8	40	61·8

Acetone (Earp and Glasstone, J., 1935, 1720); $[R_L]_D = 16{\cdot}1$; $P_{E+A} = 16{\cdot}9$.

c_2.	P_{S_2}.	P_{S_1}.	P_{S_2} [calc. by (4)].
0·00000	188	28·3	188
0·04186	161	29	161
0·09496	136	31	136
0·20665	104	36	104
0·35814	82	46	81
0·57880	70	54	70
0·75685	66	61	66
0·89866	64	66	64
0·97431	64	68	64
1·00000	63·9	68	63·9

Ethyl ether (Earp and Glasstone, J., 1935, 1709); $[R_L]_D = 22{\cdot}5$; $P_{E+A} = 23{\cdot}6$.

c_2.	P_{S_2}.	P_{S_1}.	P_{S_2} [calc. by (4)].
0·00000	62	28·3	62
0·03862	61	28·3	61
0·06053	60	28·4	60
0·11003	59	28·5	59
0·15809	58·5	28·6	58·5
0·20399	57·7	28·7	57·7
0·26413	57·2	28·8	56·8
0·32161	56·8	29·0	56·0
0·44406	56·2	29·4	54·9
0·48548	56·1	29·5	54·6
0·58144	55·7	30	54·1
0·70024	55·3	31	54·0
0·81740	55·0	33	54·1
0·90979	54·8	34	54·4
1·00000	54·7	35	54·7

The values of Z and Y for the seven substances investigated are given in Table II, and it will be seen that they are the intercepts (less P_{E+A}) given by expression (4) on the P_S axis where $\varepsilon = \infty$ and 1, or, more conveniently for graphical representation, where $1/\varepsilon = 0$ and 1. For carbon tetrachloride, $Y = 0$, and it follows that $Z(\varepsilon - 1)^4/(\varepsilon + 2)^4$ is an additional term in the distortion polarisation of the liquids involved in these solutions, and hence that Y/ε is their orientation polarisation. When $\varepsilon = \varepsilon_1$ (ε_1 being the dielectric constant of the non-polar component) and $P_S = P_\infty$, as in the infinitely dilute solution, or, for carbon tetrachloride, as in the pure liquid (here $P_S = P_1$), the second term of the expression (4) is negligible, so that

$$Y/\varepsilon_1 = P_\infty - P_{E+A} \text{ (approx.)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Further examination of the data shows that within the limits of experimental error

$$(Y/P_O - 1)/[\sqrt[4]{(Z + P_{E+A})/P_{E+A}} - 1] = 3{\cdot}25 \quad . \quad . \quad . \quad . \quad (6)$$

Even in the case of carbon tetrachloride, where both Y and P are zero, this ratio can be calculated by making use of the relation between $(P_\infty - P_{E+A})/P_O$ and molecular symmetry elaborated by Higasi (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 284), from which it may be assumed that for an isotropic substance such as carbon tetrachloride, although both sides of the expression are zero, yet in the limit $P_\infty - P_{E+A} = P_O$ and hence from (5), $Y/P_O = \varepsilon_1$. Moreover, it follows from (5) that Y/P_O is very nearly ε_1 times the ratio $(P \quad - P_{E+A})/P_O$, which Higasi found to be connected with the relationship between the direction of the dipole and the direction and magnitude of the molecular axes. Thus $Y/\varepsilon_1 P_O$ and Z/P_{E+A}, which are listed in Table II, express the extent to which the orientation and the distortion polarisation respectively are modified by induction.

TABLE II.

$t = 20°$.

	Z.	Y.	Value of (6).	$\frac{Z}{P_{E+A}}$.	$\frac{Y}{\varepsilon_1 P_O}$.*	μ [calc. by (7)].	μ (vapour).
Nitrobenzene	56	733	3·49	1·62	0·84	4·30	4·23
Chlorobenzene	64	115	2·93	1·95	0·90	1·65	1·69
Ethyl benzoate	104	176	3·54	2·32	0·94	1·99	1·95
Carbon tetrachloride	72	0	3·25	2·61	1·00	0	0
Acetone	50	383	3·08	2·98	1·05	2·79	2·84
Methylene chloride	59	118	3·04	3·45	1·11	1·50	1·53
Ethyl ether	154	84	3·08	6·51	1·40	1·13	1·14

P_O in (6) (col. 4) is the vapour value taken from the literature.
P_O in col. 6 is calculated by expression (7).
* This ratio is approximately the same as $(P_\infty - P_{E+A})/P_O$.

From the relation (6) it follows that

$$P_O = Y/[3{\cdot}25\sqrt[4]{(Z + P_{E+A})/P_{E+A}} - 2{\cdot}25] \quad . \quad . \quad . \quad . \quad . \quad (7)$$

whence the moment may be calculated in the usual manner. The values obtained are included in Table II with the comparable moments obtained from measurements on the vapours. Finally, it must be stated that P_{E+A} has been taken as 5% greater than $[R_L]_D$ because this gives very closely the known value of P_{E+A} in the case of carbon tetrachloride, but it is evident that uncertainty regarding the value of P_A, and, indeed, the probability that both P_E and P_A vary with the dielectric constant of the mixture, must undoubtedly be a source of error in the values of μ from both vapour and solution data.

EXPERIMENTAL.

Density, dielectric constant, and temperature were measured as previously described (Goss, J., 1933, 1343; 1935, 730).*

Purification of Materials.—Carbon tetrachloride. An 'AnalaR' sample was fractionally distilled, and the middle portion collected. It was dried over calcium chloride and again fractionally distilled. The middle fraction had a b. p. range of less than 0·1°.

Chlorobenzene. This was shaken with dilute sulphuric acid, washed with sodium hydroxide solution and distilled water, dried over calcium chloride, and fractionally distilled. The middle fraction boiled at constant temperature.

Ethyl benzoate. This was washed with sodium carbonate solution, shaken several times with distilled water, and dried over potassium carbonate. A final purification was effected by fractionation under reduced pressure and separation of the middle fraction.

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* The method of calibrating the condenser, there attributed to Piekara (*Bull. Acad. Polonaise*, 1933, *A*, 305), had previously been described by Smith (*Proc. Roy. Soc.*, 1932, *A*, **136**, 251).

Results.—The experimental data and the polarisations (P_{12}) calculated therefrom are recorded in Table III.

TABLE III.

c_2.	ϵ.	$d^{20°}_{4°}$.	P_{12}.	c_2.	ϵ.	$d^{20°}_{4°}$.	P_{12}.
Chlorobenzene.				*Ethyl benzoate.*			
0·00000	2·2324	1·5942	28·10	0·00000	2·2348	1·5940	28·14
0·00806	2·2593	1·5901	28·54	0·00645	2·2685	1·5890	28·76
0·01531	2·2849	1·5865	28·96	0·01351	2·3039	1·5832	29·43
0·03142	2·3371	1·5782	29·80	0·03413	2·4069	1·5669	31·32
0·04812	2·3917	1·5699	30·65	0·05252	2·5020	1·5526	33·01
0·08478	2·5142	1·5515	32·50	0·06868	2·5828	1·5404	34·43
0·18906	2·8640	1·4978	37·36	0·10835	2·7811	1·5107	37·83
0·47942	3·8257	1·3544	48·00	0·18000	3·0935	1·4600	43·12
0·89470	5·2867	1·1557	59·49	0·41006	4·0944	1·3173	58·17
1·00000	5·6483	1·1063	61·81	0·67061	5·0516	1·1800	73·69
				1·00000	6·0171	1·0463	89·78

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