# 139. *The Magnitude of the Solvent Effect in Dipole-moment Measurement. Part II. Resolution of the Solvent Effect into its Contributory Factors.*

By Frank R. Goss.

Analysis of the dielectric polarisation of certain binary mixtures of polar with non-polar liquids shows that the solvent effect can be resolved into contributions depending on the anisotropy of the electrical field which varies with the shape of non-spherical molecules, and on induction effects related to the dielectric constant of the liquids and arising both from the reaction field and from permanent dipoles. A linear relationship has been established between the field anisotropy contribution and the ratio of the axes of the polarisation ellipsoid which defines the electrical dimensions of the molecule. By assuming, in the usual manner, an approximate and average value for the atom polarisation, it is possible by a series of formulæ to rectify the observed polarisation in the liquid state for each, in turn, of the three contributions to the solvent effect, and so to obtain a corrected value for the polarisation of the liquid. This, in conjunction with the value, for the corresponding vapour, obtained by making similar approximations concerning the atom polarisation, yields by a suitable relation the atom and the orientation polarisations, together with the dipole moment, free from any error due to the above approximation.

An examination of the dielectric properties of a number of binary liquid mixtures (cf. Goss, J., 1937, 1915) has led to the conclusion that the solvent effects, *i.e.*, the amounts by which the polarisations of liquids differ from those of the corresponding vapours, can be represented in many cases by the solvent-effect equation (1) and the intercept ratio (2):

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

$$(Y/P_O - 1)/[\sqrt[4]{(Z + P_{E+A})/P_{E+A}} - 1] = V \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here $P_{E+A}$ and $P_O$ have their usual significance as the distortion and the orientation polarisation, of which the true values are assumed to be those of the vapour; $P_S$ is the partial molar polarisation of the liquid when mixed, at molar concentration $c_2$, with a non-polar and electrically isotropic liquid such as carbon tetrachloride, the evaluation of $P_S$ being made by the intercept method; $Z$ and $Y$ are constants characteristic of each polar liquid and are calculated by means of expression (1) and appropriate values of $P_S$ and the dielectric constant of the mixture; they are seen to be intercepts (less $P_{E+A}$) of the curve of $P_S$ plotted against $1/\varepsilon$ on the axes where $1/\varepsilon$ has the values 0 and 1 respectively; $V$ is a ratio varying, according to data given previously (*loc. cit.*, Table II, col. 4), from 2·93 for chlorobenzene to 3·54 for ethyl benzoate, the average value being 3 (the value previously used having been recalculated in the light of new experimental data).

The solvent-effect equation (1) is valid, apart from minor deviations (*loc. cit.*, p. 1918) attributable (see below) to anisotropy of the electrical field and which are indeed dependent on the dimensions of the molecule: it has been verified in the case of all compounds in which hydrogen bonds are absent and for which data are available; these compounds are listed in Table I.

Many authors have made theoretical predictions of the magnitude of this solvent effect, and have approached the problems from several angles. An attempt by Cowley and Partington (J., 1936, 1184) to adjudicate experimentally between certain of these theories led them to conclude that "agreement between the observed and calculated values is fairly satisfactory, although in no case are the experimental data exactly reproduced" (see also Smyth and Walls, *J. Chem. Physics*, 1935, **3**, 557; Thompson, J., 1937, 1051). Debye (*Physikal. Z.*, 1935, **36**, 100) has considered the restriction on free rotation of molecules in the liquid state, while the effect produced by the shape of the molecule can be accounted for on the basis of the theory of Raman and Krishnan (*Proc. Roy. Soc.*, 1928, *A*, **117**, 589), at least in so far as order of magnitude (cf. Mueller, *Physical Rev.*, 1936, **50**, 547; Jenkins and Bauer, *J. Amer. Chem. Soc.*, 1936, **58**, 2435) and sign (cf. Higasi, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 284; *Bull. Inst. Phys. Chem. Res.*, 1934, **13**, 1167; Frank, *Proc. Roy. Soc.*, 1935, *A*, **152**, 171) are concerned. The effect due to the mutual interaction of dipoles in close proximity has been discussed for spherical molecules by Onsager (*J. Amer. Chem. Soc.*, 1936, **58**, 1486). Although none of these theories taken alone would appear to afford a rigorous treatment of all the factors contributing to the solvent effect, each nevertheless illuminates some aspect of an admittedly formidable problem. The empirical interpretation of the solvent effect elaborated in this communication is based on the experimental data in conjunction with certain principles which underlie these theories.

TABLE I.

*Polarisation constants of carbon tetrachloride solutions at 20°.*

| | Exptl. polarisation coeffs. | | Derived polarisation coeffs. | | | Field anisotropy contribution. | Ratio of polarisation axes. Electrical. | Ratio of polarisation axes. Optical. | Dipole moment. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $P_{E+A} =$ 1·05$[R_L]_D$. | $P_\infty$. | $Z$, calc. by (1). | $Y$, calc. by (1). | $P_O$, calc. by (7). | $P_\infty - P_{E+A} - P_O$. | $K_1$, calc. by (4). | $K_2$,* calc. by (3). | $\mu$, calc. from (7). | $\mu$, vapour. |
| Quinoline | 44·0 | 146·2 | 62 | 228 | 131·8 | −29·6 | 1·79 | — | 2·50 | — |
| Bromobenzene | 35·6 | 85·7 | 53 | 111 | 62·8 | −12·7 | 1·74 | — | 1·73 | 1·71 |
| Nitrobenzene | 34·3 | 364·5 | 56 | 733 | 403·9 | −73·7 | 1·68 | 1·69 | 4·38 | 4·23 |
| Chlorobenzene | 32·8 | 84·6 | 64 | 115 | 59·4 | − 7·6 | 1·54 | 1·53 | 1·68 | 1·69 |
| Ethyl benzoate | 44·7 | 124·1 | 104 | 176 | 85·8 | − 6·4 | 1·39 | — | 2·02 | 1·95 |
| Ethyl bromide | 20·1 | 98·0 | 57 | 174 | 79·1 | − 1·2 | 1·20 | — | 1·94 | 2·01 |
| Acetone | 16·9 | 188·2 | 50 | 383 | 171·4 | − 0·1 | 1·15 | 1·19 | 2·85 | 2·84 |
| Methylene chloride | 17·1 | 70·0 | 59 | 118 | 49·8 | 3·1 | 0·99 | — | 1·54 | 1·53 |
| Chloroform | 22·5 | 49·9 | 101 | 60 | 23·1 | 4·3 | 0·70 | 0·74 | 1·05 | 1·02 |
| *iso*Propyl ether | 33·3 | 76·0 | 217 | 93 | 31·5 | 11·2 | 0·22 | — | 1·22 | — |
| Ethyl ether | 23·6 | 62·1 | 154 | 84 | 28·2 | 10·3 | 0·22 | 0·84 | 1·16 | 1·18 |

* From Stuart, "Molekülstruktur," 1934, p. 221.

The solvent-effect equation (1) and the intercept ratio (2), when compared for a number of liquids, make it possible to resolve the solvent effect into its component parts, which can each be attributed to the manner in which some specific property of the liquid state differs from that of the vapour. First, the effect of the inequality in length of the axes of the molecules will, owing to the greater proximity of molecules in the liquid, have a greater distorting effect on the external field, as is postulated by Raman and Krishnan (*loc. cit.*), and this will cause a *field anisotropy contribution.* Secondly, in accordance with the theoretical analysis of Onsager (*loc. cit.*), there will be an enhancement of the polarisation due to the field which acts upon the dipole as a result of displacements induced in the surrounding medium by the polarisation of the molecule itself. Onsager calls this the reaction field, and the effect may be termed the *reaction field contribution* to the solvent effect. Thirdly, there will be the effect arising from the moments induced in the polar molecule by other permanent dipoles; this corresponds to the induced moment due to Onsager's cavity field and will be called the *induced moment contribution.*

*Field anisotropy contribution.* Calculations of the anisotropy of the polarisation field in a liquid, carried out, amongst others, by Higasi (*loc. cit.*), indicate that the polarisation of the polar components of such binary mixtures as are now being considered is dependent on the relative lengths of the axes of the polar molecule regarded as a polarisation ellipsoid; these dimensions are not necessarily identical with those of the axes determined in other ways. From a consideration of the solvent effect in typical cases (see data for ethyl bromide and chloroform, Figs 1 and 2), and in particular of the deviation of ($P_{\infty} - P_{\mathrm{E+A}}$) from $P_{\mathrm{O}}$ and of the experimental values of $P_{\mathrm{S}}$ from those calculated by the solvent-effect equation (1), it is immediately to be seen from Table I, col. 7, that these effects as exemplified by the expression $P_{\infty} - P_{\mathrm{E+A}} - P_{\mathrm{O}}$ are positive or negative according as the dipole of the substance concerned lies along one of the minor axes or along the major axis. This rule is of general application and can be employed as the basis for a convenient empirical expression, whereas the theoretical considerations developed by Higasi (*loc. cit.*) and others, while indicating a solvent effect of the same order, cannot precisely interpret the experimental values, for, as Govinda Rau (*Proc. Ind. Acad. Sci.*, 1935, **1**, 498) has pointed out, the anisotropic field constants can only be roughly estimated. By the transformation of the solvent-effect equation previously carried out (Goss, *loc. cit.*, p. 1918) the ratio $Y/\varepsilon_1 P_{\mathrm{O}}$ is seen from Part I, Table II, to express the ratio $K$ of the dimensions of the polarisation ellipsoid of which $b_1$ is the polar axis, $b_2$ and $b_3$ the other axes, and for which some values are given in this paper (Table I, col. 9) :

$$K_2 = 2b_1/(b_2 + b_3) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This ratio of the molecular axes bears, at any rate to a first approximation, a linear relation to the ratio $Y/\varepsilon_1 P_{\mathrm{O}}$ which may be expressed as in (4).

$$K_1 = 4 - 2{\cdot}85\ Y/\varepsilon_1 P_{\mathrm{O}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Values of $K_1$ given by expression (4) from dielectric data are given in Table I and are comparable with the corresponding values of $K_2$ derived from Stuart's optical data (*op. cit.*) in accordance with the expression (3) due to Higasi (*loc. cit.*). The coefficient $K_1$ is the most convenient method of expressing the magnitude of the field anisotropy contribution to the solvent effect. It is directly related to the structure of the molecules concerned. For example, bromobenzene, in which the polar axis is obviously longer than in chlorobenzene, has a higher value of $K_1$. It is hoped to give evidence of the precise relationship which appears to exist between $K_1$ and structure in later communications.

Although it would seem that no theoretical treatment based on the anisotropy of the field can completely express the experimental results obtained for these binary mixtures, that of Govinda Rau (*loc. cit.*) based on the Raman–Krishnan theory gives values which are of the correct sign and order of magnitude (see above). His equation for the polarisation of the polar component of a binary mixture may be written as

$$P_2 = P_1 + \frac{P_{12} - P_1}{c_2} - N\Psi_1\left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\right)\left(1 - \frac{1}{c_2}\right) - \frac{\varepsilon - 1}{\varepsilon + 2} N\left(\Psi_2 + \frac{\Theta}{3kT}\right) \quad (5)$$

This treatment is based on the assumption that $P_1$ is independent of concentration, and it cannot be rigorously applied to polarisations calculated by the intercept method (cf. Goss, *loc. cit.*, p. 1916). Govinda Rau points out, too, that the anisotropic field constants $\Psi'_1$, $\Psi'_2$, and $\Theta$ in this equation will vary with the composition of the mixture. The last term does not apply over the entire range of $\varepsilon$ (cf. Goss, J., 1935, 502) for this reason, but it is evident from the experimental results that, when different polar components are compared in the same solvent at the same value of $\varepsilon$, this term expresses from a theoretical viewpoint the same relationship between structure and polarisation as is given in the equation (4).

Apparent discrepancies between the experimental values of $P_{S_2}$ and those calculated by the solvent-effect equation (1), which are recorded in Part I of this series (Goss, J., 1937, 1915, Table I) and in this paper (Table II) are of the same signs and relative magnitude in each case as the field anisotropy contribution $P_\infty - P_{E+A} - P_O$ and are presumably associated with the same anisotropy field constants. These constants will vary with the concentration of the mixture so that the effect produced cannot be precisely expressed but is in general sufficiently small to be neglected without the introduction of any serious error.

The term of Govinda Rau's equation which involves $\Psi'_1$ depends on the non-polar component and is invariably negative. This is in agreement with the experimental data; the values of $P_{S_2}$ for mixtures of polar liquids with anisotropic non-polar liquids (*i.e.*, other than carbon tetrachloride) are for identical values of $\varepsilon$ always lower than those obtained with carbon tetrachloride itself, even when the $P_\infty$ values may not be in this order. This is exemplified in the case of the mixture of ethyl bromide and hexane, for which the appropriate values are given in Table II and Fig. 1. Here, although $P_\infty$ for the hexane

TABLE II.

*Partial molar polarisations at 20°.*

$C_6H_5Br$ in $CCl_4$ (Das and Roy, *Indian J. Physics*, 1930, **5**, 441); $[R_L]_D = 33{\cdot}9$; $P_{E+A} = 35{\cdot}6$.

| $c_2$. | $P_{S_2}$. | $P_{S_1}$. | $P_{S_2}$.* |
|---|---|---|---|
| 0·00000 | 86 | 28·2 | 86 |
| 0·01001 | 85 | 28·3 | 85 |
| 0·02049 | 84 | 28·3 | 84 |
| 0·04110 | 83 | 28·3 | 83 |
| 0·04893 | 82 | 28·4 | 82 |
| 0·06420 | 82 | 28·4 | 82 |
| 0·07837 | 81 | 28·5 | 81 |
| 0·08770 | 80 | 28·6 | 80 |
| 0 1098 | 79 | 29 | 79 |
| 0·2020 | 75 | 29 | 75 |
| 0·4000 | 69 | 31 | 69 |
| 0·6000 | 66 | 34 | 66 |
| 0·8000 | 63 | 39 | 64 |
| 1·0000 | 62·8 | 43 | 62·8 |

EtBr in $C_6H_{14}$ (Smyth and Morgan, *J. Amer. Chem. Soc.*, 1928, **50**, 1547); $P_{E+A}$ (hexane) = 28·9.

| $c_2$. | $P_{S_2}$. | $P_{S_1}$. | $P_{S_1}$.* |
|---|---|---|---|
| 0·0000 | 100 | 29·3 | 29·3 |
| 0·0309 | 97 | 29·4 | 29·5 |
| 0·0783 | 92 | 29·7 | 29·8 |
| 0·1767 | 84 | 30·7 | 30·7 |
| 0·3395 | 73 | 34 | 34 |
| 0·5073 | 64 | 39 | 39 |
| 0·7188 | 58 | 49 | 49 |
| 1·0000 | 54·3 | 67 | 67 |

$COMe_2$ in *cyclo*hexane (Earp and Glasstone, J., 1935, 1720); $P_{E+A}$ (*cyclo*hexane) = 27·3.

| $c_2$. | $P_{S_2}$. | $P_{S_1}$. | $P_{S_1}$.* |
|---|---|---|---|
| 0·00000 | 180 | 27·7 | 27·7 |
| 0·04599 | 160 | 28 | 28·3 |
| 0·12911 | 133 | 30 | 29·9 |
| 0·33234 | 95 | 40 | 40 |
| 0·55818 | 74 | 56 | 56 |
| 0·82135 | 66 | 74 | 74 |
| 1·00000 | 63·9 | 84 | 84 |

$C_9H_7N$ in $CCl_4$ (Earp and Glasstone, J., 1935, 1720); $[R_L]_D = 41{\cdot}9$; $P_{E+A} = 44{\cdot}0$.

| $c_2$. | $P_{S_2}$. | $P_{S_1}$. | $P_{S_2}$.* |
|---|---|---|---|
| 0·00000 | 146 | 28·3 | 146 |
| 0·03217 | 137 | 28·4 | 137 |
| 0·12050 | 120 | 30·1 | 119 |
| 0·24647 | 105 | 34·3 | 104 |
| 0·38850 | 95 | 39·1 | 95 |
| 0·53670 | 90 | 43·2 | 90 |
| 0·67462 | 88 | 46·2 | 88 |
| 0·83162 | 87 | 49 | 87 |
| 0·95452 | 87 | 51 | 87 |
| 1·00000 | 86·7 | 52 | 86·7 |

$Pr^{\beta}_2O$ in $CCl_4$ (Earp and Glasstone, J., 1935, 1709); $[R_L]_D = 31{\cdot}7$; $P_{E+A} = 33{\cdot}3$.

| $c_2$. | $P_{S_2}$. | $P_{S_1}$. | $P_{S_2}$.* |
|---|---|---|---|
| 0·00000 | 76 | 28·3 | 76 |
| 0·06916 | 75 | 28·4 | 75 |
| 0·15477 | 74 | 28·5 | 73 |
| 0·26390 | 73 | 28·7 | 72 |
| 0·40649 | 72 | 29·1 | 70 |
| 0·50208 | 71·5 | 29·5 | 69·3 |
| 0·65893 | 70·8 | 30·3 | 69·2 |
| 0·80056 | 70·4 | 31·1 | 69·4 |
| 0·91995 | 70·3 | 32·2 | 69·8 |
| 1·00000 | 70·2 | 32·5 | 70·2 |

$CHCl_3$ in $C_6H_{14}$ (Smyth and Morgan, *loc. cit.*); $P_{E+A}$ (hexane) = 28·9.

| $c_2$. | $P_{S_2}$. | $P_{S_1}$. | $P_{S_1}$.* |
|---|---|---|---|
| 0·0000 | 50·1 | 29·3 | 29·3 |
| 0·0517 | 49·7 | 29·3 | 29·4 |
| 0·1277 | 49·2 | 29·4 | 29·6 |
| 0·2862 | 48·2 | 30 | 30·1 |
| 0·4953 | 47·0 | 31 | 31·6 |
| 0·6856 | 46·0 | 32 | 34 |
| 0·7803 | 45·6 | 34 | 36 |
| 1·0000 | 44·7 | 39 | 42 |

EtBr in $CCl_4$ (see Table IV); $[R_L]_D = 19{\cdot}1$; $P_{E+A} = 20{\cdot}1$.

| $c_2$. | $P_{S_2}$. | $P_{S_1}$. | $P_{S_2}$.* |
|---|---|---|---|
| 0·00000 | 98 | 28·2 | 98 |
| 0·01326 | 96 | 28·2 | 96 |
| 0·02255 | 95 | 28·3 | 95 |
| 0·03601 | 93 | 28·3 | 93 |
| 0·04647 | 91 | 28·3 | 91 |
| 0·08538 | 86 | 28·6 | 87 |
| 0·12218 | 83 | 29·1 | 83 |
| 0·23730 | 73 | 31 | 73 |
| 0·55515 | 59 | 40 | 59 |
| 0·79674 | 56 | 46 | 56 |
| 1·00000 | 55·3 | 53 | 55·3 |

$CHCl_3$ in $CCl_4$ (see Table IV); $[R_L]_D = 21{\cdot}4$; $P_{E+A} = 22{\cdot}5$.

| $c_2$. | $P_{S_2}$. | $P_{S_1}$. | $P_{S_2}$.* |
|---|---|---|---|
| 0·00000 | 49·9 | 28·2 | 49·9 |
| 0·01308 | 49·7 | 28·2 | 49·7 |
| 0·02441 | 49·5 | 28·2 | 49·5 |
| 0·03582 | 49·3 | 28·2 | 49·3 |
| 0·06035 | 49·0 | 28·2 | 48·9 |
| 0·11545 | 48·5 | 28·3 | 48·1 |
| 0·16822 | 48·0 | 28·4 | 47·4 |
| 0·33779 | 47·0 | 28·7 | 45·5 |
| 0·54269 | 46·0 | 29·5 | 44·1 |
| 0·78471 | 45·2 | 30·9 | 43·8 |
| 1·00000 | 44·8 | 33·0 | 44·8 |

$C_6H_5Cl$ in $C_6H_{14}$ (Smyth and Morgan, *loc. cit.*); $P_{E+A}$ (hexane) = 28·9.

| $c_2$. | $P_{S_2}$. | $P_{S_1}$. | $P_{S_1}$.* |
|---|---|---|---|
| 0·0000 | 83 | 29·3 | 29·3 |
| 0·1068 | 79 | 29·5 | 29·8 |
| 0·2132 | 75 | 30·6 | 30·6 |
| 0·3798 | 70 | 33 | 33 |
| 0·6458 | 65 | 38 | 38 |
| 1·0000 | 61·8 | 48 | 48 |

* Calculated by (1).

solution is higher than that for carbon tetrachloride, the values of $P_{S_2}$ for the former are for the same values of $\varepsilon_1$ always lower than for the latter. In the same way, values of $P_{S_1}$ for the non-polar components of the binary mixtures are above or below the average values calculated in accordance with the solvent-effect equation (1) according as the field anisotropy contribution of the polar component is negative or positive (see Table II).

*Reaction field contribution.* Those parts of the solvent effect which do not depend directly on the dimensions of the polarisation ellipsoid of the polar molecules are expressed in the

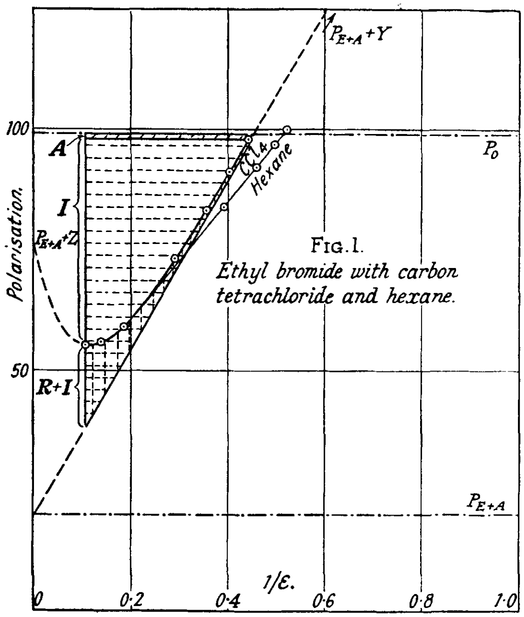


FIG. 1. *Ethyl bromide with carbon tetrachloride and hexane.*

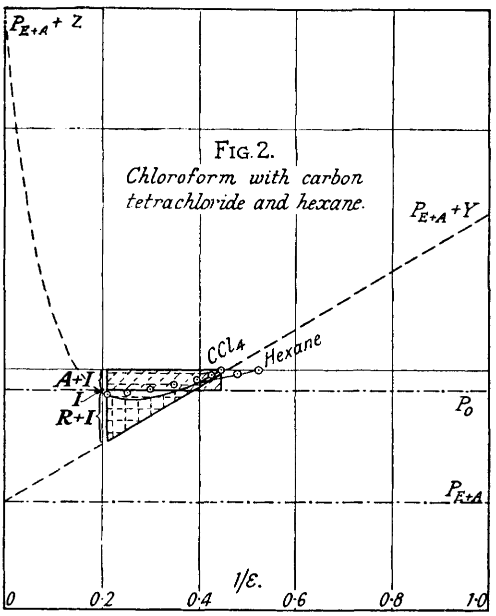


FIG. 2. *Chloroform with carbon tetrachloride and hexane.*

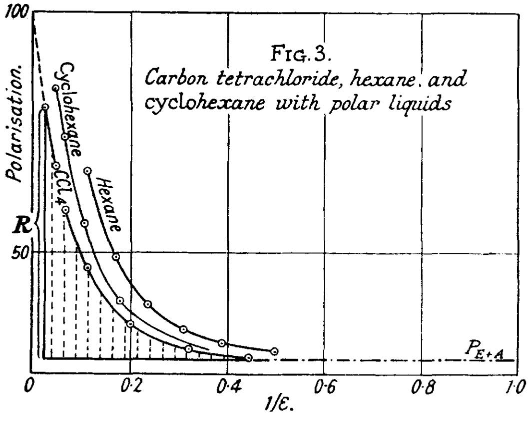


FIG. 3. *Carbon tetrachloride, hexane, and cyclohexane with polar liquids*

*Partial molar polarisations,*
$P_S = P_{E+A} + Z(\varepsilon-1)^4/(\varepsilon+2)^4 + Y/\varepsilon$,
*extrapolated to* $\varepsilon = 1$ *and* $\varepsilon = \infty$,
*for binary liquid mixtures.*

*Experimental curves* ................ —○—
*Corresponding vapour polarisations.* —·—
*Solvent effect:*
*Field anisotropy contribution*, **A** ▨
*Reaction field contribution*, **R** ⁞
*Induced moment contribution*, **I** ☰

two variable terms of the solvent-effect equation (1), the first of which, $Z(\varepsilon - 1)^4/(\varepsilon + 2)^4$, is common to both polar and non-polar molecules, data for binary mixtures containing hexane and *cyclo*hexane as well as for carbon tetrachloride and polar molecules being included in Table II and Figs. 1—3. This term may therefore be interpreted as an induction effect, $Z(\varepsilon - 1)^4/(\varepsilon + 2)^4$, associated with the reaction of the electric field to the polarisation (cf. Onsager, *loc. cit.*) and hence dependent on the volume polarisability $(\varepsilon - 1)/(\varepsilon + 2)$ of the medium. It may be seen that the ratio of this induced contribution to the normal distortion polarisation, which may be represented by $Z/P_{E+A}$, is related to the dimensions of the molecule, the incidence of this reaction field contribution increasing as the polar axis becomes relatively shorter; in fact, by combining equations (2) and (4) it is seen that

$$K_1 = 6{\cdot}55 - 3{\cdot}82\sqrt[4]{(Z + P_{\mathrm{E+A}})/P_{\mathrm{E+A}}} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

*Induced moment contribution.* When allowance has been made for the contributions already considered, the remaining part of the solvent effect, which has a finite value only in the case of polar molecules, and is expressed by the $Y/\varepsilon$ term of the solvent-effect equation (1), can be attributed to the polarisation induced by the permanent dipoles. It is necessarily zero for the infinitely dilute solution and, as already stated, for non-polar components. This induced moment contribution forms, however, the largest part of the solvent effect in the case of polar molecules, as can be seen from Figs. 1 and 2.

*Calculation of dipole moments and elimination of uncertainty in the atom polarisation value.* These several contributions into which the solvent effect has been resolved can only be allowed for in evaluating dipole moments from solution data if $Y$ and $Z$ are obtained for this purpose from the experimental values of $P_{\mathrm{S}_2}$ by means of the solvent-effect equation (1). These constants are employed to calculate $P_{\mathrm{O}}$ by means of the intercept expression (2). This is expressed in (7), which is a more exact form of the expression for $P_{\mathrm{O}}$ given in Part I of this series.

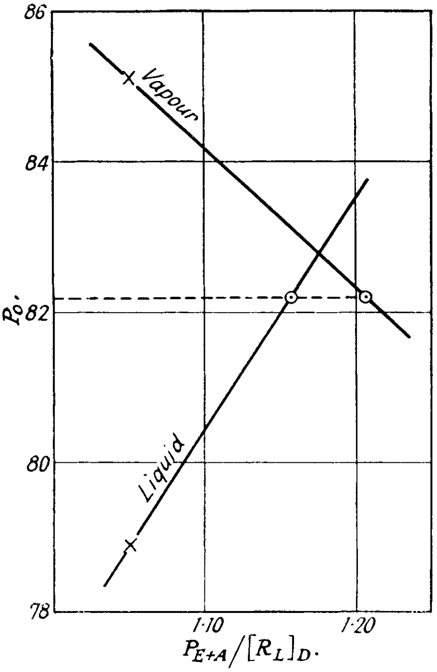
$$P_{\mathrm{O}} = Y/[3\sqrt[4]{(Z + P_{\mathrm{E+A}})/P_{\mathrm{E+A}}} - 2] \quad . \quad . \qquad (7)$$

Now the moment may be calculated in the usual manner. In Table II some new determinations of $P_{\mathrm{S}_1}$ and $P_{\mathrm{S}_2}$ are given, new experimental values of $P_{12}$ and data from the literature being used. From this and similar data given in Part I of this series, comparative values of the dipole moment have been calculated and are included in Table I.

Differences between the moments calculated from the liquid and the vapour data have already been attributed (Goss, *loc. cit.*) to uncertainty in the magnitude of the atom polarisation ($P_{\mathrm{A}}$) which has been assessed by Sugden (J., 1937, 1779) at a mean value of $1{\cdot}05[R_L]_{\mathrm{D}}$ for vapours; it has been put at the same figure for the liquids in Part I of this series because, by using that value rather than a higher or a lower one, better average agreement was obtained between the liquid moments and those for the vapour obtained from the variation of polarisation with temperature. Now it is evident that $P_{\mathrm{A}}$ cannot always be equal to $1{\cdot}05\ [R_L]_{\mathrm{D}}$ (cf. Finn, Hampson, and Sutton, J., 1938, 1254) and also that in the comparison of vapour and liquid values of the moments in Table I there are certain discrepancies which although small are nevertheless quite definite and cannot reasonably be attributed to experimental error. As an example the case of ethyl bromide may be taken. Higasi (*loc. cit.*, p. 300) has already noted that such a discrepancy may exist in the case of the alkyl halides and has suggested that the volatility of these substances may cause an error in the measured concentration of the liquid mixtures. However, the measurements for ethyl bromide recorded in this paper have been carried out with especial care to avoid such an error, and an exactly similar discrepancy has been found for higher and less volatile alkyl halides (unpublished observations). Calculations have consequently been made to ascertain the manner in which the apparent value of $P_{\mathrm{O}}$ varies with a change in the

FIG. 4.

*Variation of calculated values of $P_{\mathrm{O}}$ with assumed value of $P_{\mathrm{A}}$ for liquid and vapour ethyl bromide.*



× $P_{\mathrm{O}}$, *on the assumption that* $P_{\mathrm{E+A}}/[R_L]_{\mathrm{D}} = 1{\cdot}05$.

⊙ $P_{\mathrm{O}}$, *on the assumption that* $P_{\mathrm{E+A}}$ *(vapour)*$/P_{\mathrm{E+A}}$ *(liquid)* $= 1{\cdot}05$

assumed value of $P_A$ and it is found, as shown in Fig. 4, that in the case of ethyl bromide, as the value assumed for $P_A$ increases, $P_O$ increases for the liquid but falls for the vapour (data taken from Sugden, J., 1937, 158). Owing to the field anisotropy contribution depending on the $\Psi_2$ constant (see equation 5), the value of $P_{E+A}$ for the vapour must be greater than that for the liquid by an amount which can only be obtained directly if the molecular refraction for the vapour is known (cf. Goss, J., 1933, 1341); if, however, this amount is taken as 5% of $P_{E+A}$ on the basis of known values for non-polar molecules'(cf. Goss, J., 1935, 727) the values of $P_{E+A}$, $P_O$, and $\mu$ can be determined independently of any arbitrary assumption as to the value of $P_A$, as exemplified in Fig. 4. The values for ethyl bromide are given in Table III.

TABLE III.

*Polarisation of ethyl bromide* ($P_A$ *error eliminated*).

| | $P_{E+A}$. | $P_O$. | $\mu$. |
|---|---|---|---|
| Vapour .................... | 23·2 | 82·1 | 1·98 |
| Liquid ....................... | 22·2 | 82·1 | 1·98 |

## EXPERIMENTAL.

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

*Purification of Materials.—Carbon tetrachloride.* As previously described (Goss., J., 1937, 1919).

*Chloroform.* An " AnalaR " sample, $d_{4°}^{20°}$ 1·4779, was thoroughly washed to remove alcohol, dried twice over calcium chloride, and fractionally distilled. The middle fraction which boiled at constant temperature had $d_{4°}^{20°}$ 1·4889.

*Ethyl bromide.* This was shaken with sulphuric acid, then several times with sodium carbonate, dried with calcium chloride, and fractionally distilled. The middle portion had constant b. p.

TABLE IV.

*Polarisations at* 20°.

| *Ethyl bromide and carbon tetrachloride.* | | | | *Chloroform and carbon tetrachloride.* | | | |
|---|---|---|---|---|---|---|---|
| $c_2$. | $\epsilon$. | $d_{4°}^{20°}$. | $P_{12}$. | $c_2$. | $\epsilon$. | $d_{4°}^{20°}$. | $P_{12}$. |
| 0·00000 | 2·2383 | 1·5942 | 28·19 | 0·00000 | 2·2398 | 1·5942 | 28·22 |
| 0·01326 | 2·3004 | 1·5930 | 29·09 | 0·01308 | 2·2606 | 1·5929 | 28·49 |
| 0·02255 | 2·3443 | 1·5920 | 29·70 | 0·02441 | 2·2791 | 1·5918 | 28·73 |
| 0·03601 | 2·4073 | 1·5908 | 30·55 | 0·03582 | 2·3006 | 1·5907 | 29·01 |
| 0·04647 | 2·4566 | 1·5898 | 31·20 | 0·06035 | 2·3398 | 1·5882 | 29·50 |
| 0·08538 | 2·6420 | 1·5862 | 33·45 | 0·11545 | 2·4367 | 1·5827 | 30·66 |
| 0·12218 | 2·8289 | 1·5827 | 35·50 | 0·16822 | 2·5294 | 1·5774 | 31·69 |
| 0·23730 | 3·4178 | 1·5710 | 40·67 | 0·33779 | 2·8683 | 1·5604 | 34·97 |
| 0·55515 | 5·483 | 1·5335 | 50·37 | 0·54269 | 3·3373 | 1·5389 | 38·46 |
| 0·79674 | 7·501 | 1·4979 | 53·94 | 0·78471 | 4·025 | 1·5131 | 42·07 |
| 1·00000 | 9·613 | 1·4617 | 55·29 | 1·00000 | 4·806 | 1·4889 | 44·84 |

*Results.*—The experimental data and the polarisations ($P_{12}$) for the binary mixtures calculated therefrom are recorded in Table IV.

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