113. *The Dipole Moments of Associated Liquids.*

By Frank R. Goss.

The influence of a liquid medium in reducing the observed polarisation of a polar substance in solution was formerly ascribed (Debye, Marx's "Handbuch der Radiologie," Leipzig, 1925, VI, 633) to association of the polar molecules; Bury and Jenkins (J., 1934, 688), however, pointed out that, to accord with Sidgwick's views ("Electronic Theory of Valency," Oxford, 1927, 132), association should lead to an increase instead of a decrease in polarisation, as indeed has been experimentally observed in the case of the alcohols (cf. Smyth and Stoops, *J. Amer. Chem. Soc.*, 1929, **51**, 3312); it has further been shown (Goss, J., 1934, 696) that decrease in polarisation, where it is observed, can be explained by the effect of the anisotropy of the polarisation field. It seems possible, therefore, that the variations in the polarisation of solutes with concentration may be due to the opposing effects of anisotropy and association, causing respectively decreases and increases in the polarisation of substances in the liquid state.

We consider anisotropy first. The Clausius–Mosotti expression

$$(\varepsilon - 1)/(\varepsilon + 2) = 4\pi\nu\alpha/3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which connects the dielectric constant ε with α, the polarisability of the molecules, and ν, the number of molecules per unit volume, is theoretically valid only for a symmetrical polarisation field. It has been experimentally verified for gases (Uhlig, Kirkwood, and Keyes, *J. Chem. Physics*, 1933, **1**, 155; Michels and Michels, *Phil. Trans.*, 1934, *A*, **231**, 409) and expressed in a form applicable to an anisotropic polarisation field (Raman and Krishnan, *Proc. Roy. Soc.*, 1928, *A*, **117**, 595), *viz.*,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3}\nu\frac{\frac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3)}{1 - \frac{1}{3}\nu(\alpha_1 s_1 + \alpha_2 s_2 + \alpha_3 s_3)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where α_1, α_2, α_3 are components of α, and s_1, s_2, s_3 are the component amounts by which the polarisation field varies from the values it would have if it were isotropic.

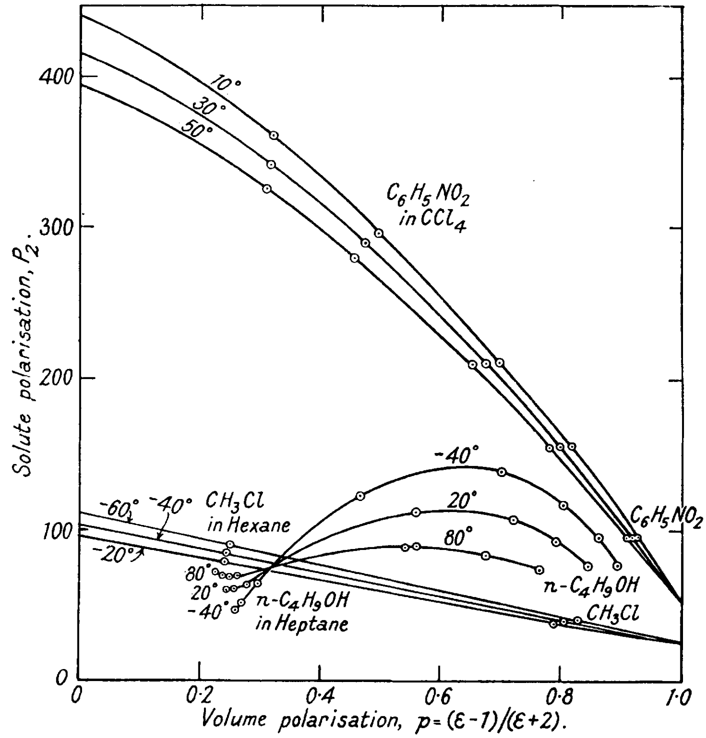
The Raman–Krishnan formulæ express in theoretical terms the experimental facts that (*a*) the electron and atom polarisations of all liquids increase slightly with temperature (cf. Goss, J., 1933, 1341), (*b*) the calculated polarisation *P* of a polar solute varies with its concentration in solution (cf. van Arkel and Snoek, *Rec. trav. chim.*, 1932, **51**, 1081), and (*c*) the polarisation of such a solute at infinite dilution *P* varies as the solvent is changed (cf. Muller, *Physikal. Z.*, 1933, **34**, 689), with the consequence that dipole moments calculated directly from solution data by Debye's formula ("Polare Molekeln," Leipzig, 1929, 56), which is based on the expression (1), may vary with the solvent, and usually differ from the moments calculated from measurements on the gaseous state (cf. Smyth, *J. Chem. Physics*, 1932, **1**, 247).

The theoretical expression for the components of the observed polarisation P_2 of a non-associating substance, either as a pure liquid or as a component of a non-associating liquid mixture, may conveniently be written (cf. Goss, *loc. cit.*)

$$P_2 = P_{E+A+O} - pA_{E+O} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where P_{E+A+O} represents the molar polarisations which the substance would have in the gaseous state, p is the polarisation of the medium per unit volume $[p = (\varepsilon - 1)/(\varepsilon + 2)]$, and A_{E+O} is the molar anisotropy factor. A_{E+O} represents the sum of two factors $A_E = -N\psi$ and $A_O = -N^2\Theta/3RT$, which are respectively the amounts by which the distortion and the orientation polarisation, P_{E+A} and P_O, are reduced by the anisotropy of the local field, ψ and Θ have the significance given in the Raman–Krishnan theory (*q.v.*), N is the Avogadro number, R is the gas constant, and T the absolute temperature. This expression can be applied to methyl chloride (see Fig. 1), but is evidently only valid for the simplest non-associating molecules.

FIG. 1.



In order to explain the polarisation of more complex substances, Sugden (*Nature*, 1934, **133**, 415) introduced an addition P_a to those terms which are independent of temperature, so that the polarisation of liquids could be expressed as

$$P_2 = P_{E+A+O} + P_a - pA_{E+O} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This formula, however, is found to be inapplicable to the published data for many substances, including ether and chloroform (Goss, *loc. cit.*), nitrobenzene (this paper), and alcohol (Smyth and Stoops, *loc. cit.*).

Subbaramaiya (*Proc. Indian Acad. Sci.*, 1934, *A*, **1**, 355) has discussed the effect of the anisotropy terms on the usual mixture rule for the polarisation of liquids, *viz.*,

$$P_{12} = P_1c_1 + P_2c_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where P_{12} is the polarisation of the mixture, P_1 that of the solvent, and c_1, c_2 the molar concentrations of the solvent and the solute respectively. It seems desirable, therefore, to consider the effect of introducing terms arising from association. If the additional polarisations arising from the association of the solvent and of the solute are represented by K_1 and K_2 respectively, and that which the solute would have if it were not associated is denoted by P'_2, then, provided K_1 be small compared with P_1,

$$P_{12} = P_1c_1 + P'_2c_2 + K_1c_1 + K_2c_2 \quad \ldots \ldots \ldots \quad (6)$$

Combining this with expression (5), we have

$$P_2 = P'_2 + K_2 - K_1c_1/c_2 \quad \ldots \ldots \ldots \ldots \quad (7)$$

Now it is evident that, for an associated liquid, expression (4) must be written as

$$P'_2 = P_{\text{E+A+O}} + P_a - pA_{\text{E+O}} \quad \ldots \ldots \ldots \quad (8)$$

whence
$$P_2 = P_{\text{E+A+O}} + P_a - pA_{\text{E+O}} + K_2 - K_1c_1/c_2 \quad \ldots \quad (9)$$

If now K_1 has a value other than zero, and the expression (9) is extrapolated to values of p for which either c_1 or c_2 is less than zero, the values obtained for the polarisation terms will have no real significance. Fairbrother (J., 1934, 1846) has shown that extrapolation of the observed relationship between P_2 and p for nitrobenzene in p-xylene solution does, in fact, lead to unexpectedly high values of $P_{\text{E+A+O}}$.

Values for the polarisation of nitrobenzene in carbon tetrachloride, which may be regarded as essentially a non-associating solvent, have been provided by Pal (*Phil. Mag.*, 1930, **10**, 265), and these can be represented very closely by $P_2 = a - (p + p^2)b/2$, *i.e.*, $P_2 = a - pb + (p - p^2)b/2$, where a and b are constants for each temperature. A comparison with equation (9) shows that, provided P_a be negligible (see below), $a = P_{\text{E+A+O}}$ and $b = A_{\text{E+O}}$, so that

$$P_2 = P_{\text{E+A+O}} - pA_{\text{E+O}} + \tfrac{1}{2}(p + p^2)A_{\text{E+O}} \quad \ldots \quad (10)$$

The values of $P_{\text{E+A+O}}$ and $A_{\text{E+O}}$ calculated from Pal's data by means of equation (10), by using the method of zero sum, are given in Table I.

TABLE I.

Polarisation of nitrobenzene.

t.	$P_{\text{E+A+O}}(p = 0)$.	$A_{\text{E+O}}$.	$P_{\text{E+A+O}} - A_{\text{E+O}}(p = 1)$.
10°	440·2	385·6	54·6
20	427·6	373·7	53·9
30	416·2	362·9	53·3
40	405·0	352·3	52·7
50	395·0	342·4	52·6

The values of P_2 calculated from these data are compared in Table II with the experimental values at 10°: there is equally good agreement between the calculated and experimental values at the other temperatures, and these lie on a series of smooth curves, which are plotted in Fig. 1.

Comparison of equations (9) and (10) shows that K_2 for nitrobenzene must have the the value $\frac{1}{2}(p - p^2)A_{\text{E+O}}$. This means that the polarisation due to the association of liquid nitrobenzene vanishes when the volume polarisation is zero or unity, and in these limiting cases the polarisation formula for nitrobenzene reduces to the expression (4). Hence the dipole moment (μ) of nitrobenzene may be calculated by a method similar to that already used in the case of non-associating liquids, *viz.*, the temperature variation of the $p = 0$ intercepts given by equation (10), and these should vary in accordance with the Debye equation, $1{\cdot}2732\sqrt{P_0T} = \mu$.

Values for the $p = 0$ and $p = 1$ intercepts at several temperatures for nitrobenzene are given in Table I, and from these a graph has been compiled (Fig. 2) to compare, at 25°, all the data given by Pal (*loc. cit.*), Fairbrother (*loc. cit.*), and Jenkins (J., 1934, 480) for nitrobenzene in several different solvents. The values for carbon tetrachloride, hexane, and decane all lie on a curve represented by expression (10), those for benzene and p-xylene

TABLE II.

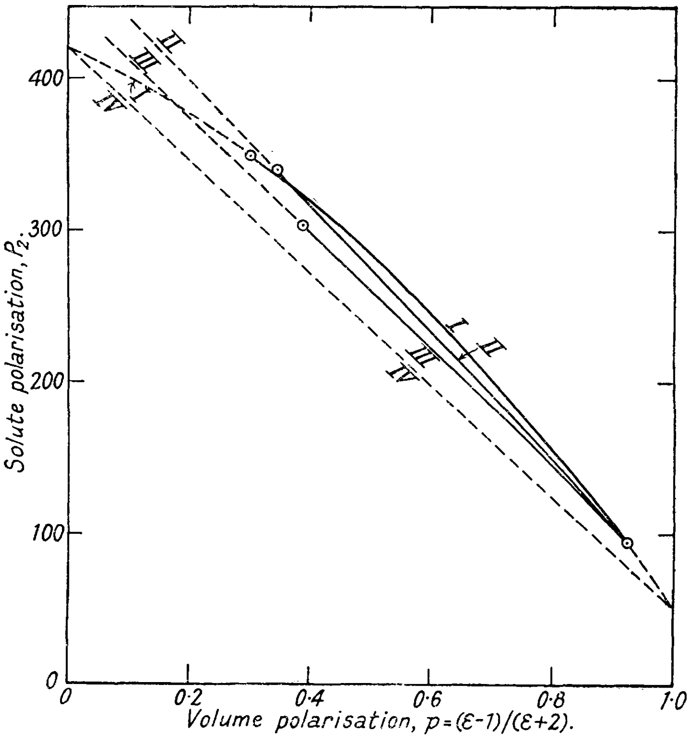
Nitrobenzene in carbon tetrachloride at 10°.

c_2.	p.*	P_2, found.*	P_2, calc.	c_2.	p.*	P_2, found.*	P_2, calc.	c_2.	p.*	P_2, found.*	P_2, calc.
—	0·0000	—	440·2	0·0959	0·5419	277·9	279·1	0·5917	0·8717	126·2	125·7
0·0099	0·3274	358·9	356·4	0·1527	0·6297	241·1	242·1	0·7166	0·8947	113·3	113·3
0·0210	0·3629	345·7	344·8	0·2098	0·6937	213·4	213·6	0·8046	0·9074	106·2	106·5
0·0319	0·3953	334·2	333·8	0·3103	0·7683	178·0	178·2	0·8936	0·9183	100·2	100·5
0·0469	0·4355	319·2	319·4	0·4039	0·8148	155·5	155·1	1·0000	0·9285	94·1	94·9
0·0706	0·4915	297·8	298·8	0·5001	0·8481	138·5	138·0	—	1·0000	—	54·6

* Pal (*loc. cit.*).

FIG. 2.

Nitrobenzene in solution at 25°.



Curve.	Solvents.	Formula.
I	CCl_4, hexane, decane	$P_2 = P_{E+A+O} - pA_{E+O} + \frac{1}{2}(p + p^2)A_{E+O}$.
II	Benzene, p-xylene	$P_2 = P_{E+A+O} - pA_{E+O} + \frac{1}{2}(p + p^2)A_{E+O} - K_1c_1/c_2$.
III	CS_2, $CHCl_3$	
IV	?	$P_2 = P_{E+A+O} - pA_{E+O}$

on a curve of the type (9), and those for carbon disulphide and chloroform on a different curve of the same type corresponding to a high value of K_1. In order to calculate the moment, it appears preferable to employ the values given by Fairbrother for decane solutions which cover a wide temperature range, in conjunction with the $p = 1$ intercepts already obtained from Pal's data, which change but slightly with temperature (Table III). In this way a value of 4·28*D* is obtained, in close agreement with Groves and Sugden's value (J., 1934, 1094) for the vapour. It will be noted that, if the basis of these calculations is correct, the invariable term of the polarisation for nitrobenzene is 38·4 c.c., very little higher than Groves and Sugden's value for P_{E+A} in the vapour state, so that the term P_a is either zero or negligibly small.

TABLE III.

Nitrobenzene in decane.

t.	p.*	$P_{E+A+O} - A_{E+O}$.†	P_2.*	P_{E+A+O}.	t.	p.*	$P_{E+A+O} - A_{E+O}$.†	P_2.*	P_{E+A+O}.
20°	0·3186	53·9	345·2	423·4	80°	0·2891	51·8	301·1	358·2
40	0·3084	52·8	329·2	399·1	100	0·2797	51·8	289·0	340·7
60	0·2986	52·1	314·2	377·2	120	0·2708	51·8	278·5	325·6

$\mu = 4{\cdot}28D$; $P_{E+A} = 38{\cdot}4$ c.c.; $P_E = 32{\cdot}0$ c.c.

* Fairbrother (*loc. cit.*). † See Table I.

An important conclusion to be drawn from expression (9) is that, in selecting data for the calculation of dipole moments, either of associating or of non-associating substances, the solvents must be such as carbon tetrachloride or the paraffin hydrocarbons, giving a zero value for K_1; this should replace the older conception that such solvents should be merely non-polar, and any confusion on this point is seen to be particularly misleading in the case of the aromatic hydrocarbons.

It will be noticed that the curves for *n*-butyl alcohol, calculated from the data of Smyth and Stoops (*loc. cit.*) and plotted in Fig. 1, are more complex than those for nitrobenzene; it is evident that K_2 for the alcohols must be a more complex function of p than it is in the case of nitrobenzene.

SUMMARY.

1. The differences observed between the dielectric polarisation of liquids and gases are attributed mainly to decreases due to the anisotropy and the association of the solvent, and to an increase due to the association of the solute.

2. A formula for the polarisation of liquids is deduced and exemplified by reference to the behaviour of nitrobenzene in various solvents.

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