407. *The Determination of Dipole Moments in Solution.*

By Fred Fairbrother.

Recent work, particularly by Müller (*Physikal. Z.*, 1932, **33**, 732; 1933, **34**, 689; 1934, **35**, 346; *Trans. Faraday Soc.*, 1934, **30**, 729) and by Jenkins (this vol., p. 480), has shown that, contrary to former belief, the dipole moment of a molecule measured in solution in the usual way is not independent of the non-polar solvent used, even although the polarisation measurements are in each case extrapolated to infinite dilution, but that as the dielectric constant of the solvent decreases the apparent moment of the solute increases.

One must distinguish between an *actual* change in effective moment when the gaseous molecule passes into solution, caused by electronic shifts or changes in valency angles, and a change in apparent moment due to the method of measurement. It is the latter with which we are concerned in the present paper.

A few attempts have been made to correlate measurements of polarisation in solution with the polarisation in the gaseous state, where this is known, with the object of utilising the former to obtain the true moment of the solute molecules. For instance, Jenkins (this vol., p. 480) finds that the total polarisation of the solute at infinite dilution obtained in the usual way, at one temperature, gives a straight line when plotted against the reciprocal of the dielectric constant of the solvent, but that extrapolation of this line to $\varepsilon = 1$, gives an improbably high value of the moment in question. Müller (*loc. cit.*) has plotted the observed moment against the dielectric constant of the solvent and obtains a series of curved lines, the curvature of which increases with the dipole moment of the solute and which flatten out as the dielectric constant of the solvent decreases, the difference between the gas value and that in hexane often being very small. Müller finds that the polarisation of a number of substances in solution relative to the value in the gaseous state can be expressed by the empirical formula

$$(P - R)_{\text{solvent}}/(P - R)_{\text{gas}} = 1 - \text{const.}\ (\varepsilon - 1)^2,$$

in which P and R are respectively the total molar polarisation and the refractivity of the substance, and the constant is equal to $0{\cdot}075 \pm 0{\cdot}005$.

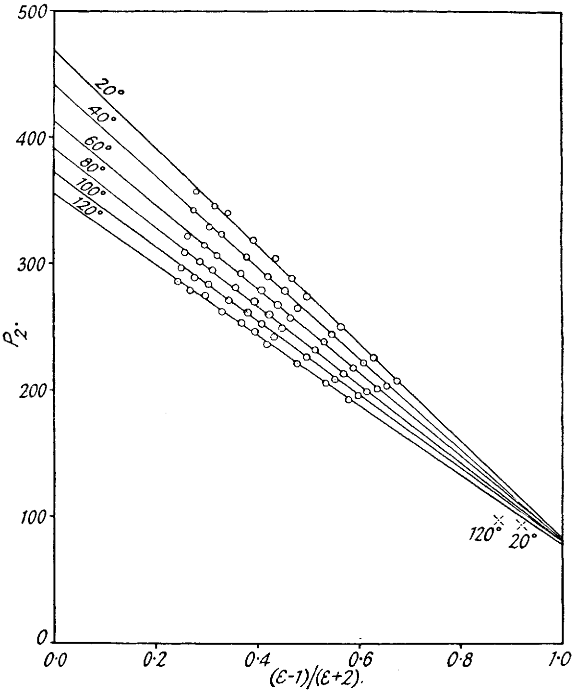
Goss (this vol., p. 696) has made use of a theoretical treatment of Raman and Krishnan (*Proc. Roy. Soc.*, 1928, *A*, **117**, 589), who have calculated the effect of the optical and dielectric anisotropy on the observed polarisations. This work will be referred to later.

Sugden (*Nature*, 1934, **133**, 415) has shown that if measured values of the molecular polarisabilities, P_2, of a solute are plotted against the corresponding values of the volume polarisability, $(\varepsilon - 1)/(\varepsilon + 2)$, for solutions of benzonitrile, nitrobenzene, and chlorobenzene in a number of non-polar solvents, the points for each substance all lie near a straight line, the slope of which is approximately equal to P_μ, that portion of the total polarisation which is due to the permanent dipoles. He suggests the formula

$$_{(\text{liq.})}P_2 = \alpha + {}_{(\text{gas})}P_2 - P_\mu(\varepsilon - 1)/(\varepsilon + 2),$$

where α is a constant. From this it follows that, if measurements were made at different temperatures in the case of a solute whose moment was independent of the temperature, the lines obtained by plotting $P_{\text{liq.}}$ against $(\varepsilon - 1)/(\varepsilon + 2)$ should converge to a common point, $P_{\text{liq.}} = \alpha + P_{\text{a}} + P_{\text{e}}$ at $(\varepsilon - 1)/(\varepsilon + 2) = 1$, that is, if the lines are extrapolated to $\varepsilon = \infty$.

Such measurements have now been made, in decane (di*iso*amyl) in order to obtain low values of $(\varepsilon - 1)/(\varepsilon + 2)$ over a wide temperature range, and in *p*-xylene. The results are given in Table I (polarisations being given in c.c.) and plotted in the fig: W_2 is the weight fraction of the nitrobenzene, ε is the dielectric constant of the solution, d its density, and P_2 the molar polarisation of the solute. The polarisations were calculated by the simplified method which does not involve the use of mol.-fractions (Sugden, *Trans. Faraday Soc.*, 1934, **33**, 720). The values of ε for pure nitrobenzene are taken from the International Critical Tables; the corresponding densities were measured in the usual way as described below.



EXPERIMENTAL.

The dielectric constants were measured at approximately 10^6 cycles per sec. by the resonance method previously described (Fairbrother, J., 1932, 43; *Proc. Roy. Soc.*, 1933, *A*, **142**, 173). Two three-plate platinum condensers were used. The first, used to measure the solvents, the solutions in decane, and the first three solutions in *p*-xylene, was as previously described and was of about 215 mμF capacity when filled with dry air. The remaining five solutions in *p*-xylene were measured in a condenser of similar construction and of approximately the same dimensions, except that the plates were 2·5 cm. long. This second condenser when filled with dry air was of about 82 mμF capacity, and as the dimensions of the lead-in wires and the positions of the condensers in the oil-bath were almost the same, no effective change in the inductance of the leads was brought about by changing from one condenser to the other. The capacity of this condenser, and the range over which the standard condenser with its leads had been calibrated, set an upper limit to the dielectric constants, and therefore to the concentrations of nitrobenzene, which could be measured.

The densities were measured in a quartz pyknometer of the Sprengel type, having a very fine-bore tip bent downwards and fitted, by means of a split cork, with a small removable glass cup to catch the liquid driven out on expansion. This cup was removed before the adjustment

TABLE I.

	Decane.			*p*-Xylene.				Decane.			*p*-Xylene.		
t.	ε.	*d*.	*P*.	ε.	*d*.	*P*.	*t*.	ε.	*d*.	*P*.	ε.	*d*.	*P*.
20°	1·983	0·7235	48·48	2·268	0·8610	36·61	80°	1·901	0·6765	48·52	2·165	0·8081	36·73
40	1·956	0·7082	48·49	2·234	0·8437	36·65	100	1·873	0·6601	48·52	2·131	0·7902	36·76
60	1·928	0·6925	48·48	2·200	0·8260	36·70	120	1·846	0·6435	48·57	2·097	0·7724	36·78

Nitrobenzene in decane.

	W_2 = 0·01885.			W_2 = 0·03767.				W_2 = 0·01885.			W_2 = 0·03767.		
t.	ε.	*d*.	P_2.	ε.	*d*.	P_2.	*t*.	ε.	*d*.	P_2.	ε.	*d*.	P_2.
20°	2·189	0·7289	357·4	2·403	0·7344	345·2	80°	2·058	0·6818	309·7	2·220	0·6872	301·1
40	2·145	0·7134	342·4	2·338	0·7188	329·2	100	2·017	0·6654	296·7	2·165	0·6706	289·0
60	2·098	0·6978	321·5	2·277	0·7033	314·2	120	1·978	0·6486	285·6	2·114	0·6538	278·5

Nitrobenzene in *p*-xylene.

	W_2 = 0·02066.			W_2 = 0·04672.				W_2 = 0·07170.			W_2 = 0·09351.		
20°	2·562	0·8664	340·1	2·941	0·8732	318·6	20°	3·330	0·8794	303·5	3·674	0·8854	288·8
40	2·500	0·8489	323·5	2·846	0·8557	305·4	40	3·192	0·8622	290·2	3·509	0·8679	278·6
60	2·441	0·8314	306·4	2·757	0·8381	292·3	60	3·072	0·8446	279·1	3·359	0·8503	268·7
80	2·386	0·8134	294·5	2·674	0·8200	281·5	80	2·964	0·8266	270·0	3·223	0·8322	260·2
100	2·334	0·7950	284·4	2·598	0·8018	271·8	100	2·861	0·8080	261·1	3·099	0·8139	252·3
120	2·283	0·7764	275·0	2·524	0·7829	262·9	120	2·766	0·7893	253·5	2·984	0·7952	245·2
	W_2 = 0·1142.			W_2 = 0·1668.				W_2 = 0·2245.			W_2 = 0·2781.		
20	3·988	0·8905	274·6	4·932	0·9055	250·0	20	6·066	0·9217	226·8	7·205	0·9374	208·0
40	3·794	0·8729	265·9	4·657	0·8878	244·2	40	5·668	0·9039	222·3	6·693	0·9194	204·9
60	3·615	0·8553	256·7	4·403	0·8701	238·0	60	5·319	0·8862	218·0	6·244	0·9017	201·7
80	3·457	0·8373	249·1	4·174	0·8523	232·3	80	5·004	0·8682	213·8	5·847	0·8835	198·8
100	3·312	0·8187	242·2	3·967	0·8337	227·0	100	4·723	0·8497	209·9	5·487	0·8650	195·9
120	3·181	0·8002	236·1	3·778	0·8149	221·1	120	4·473	0·8309	206·5	5·162	0·8460	193·2

Nitrobenzene (liquid).

t.	ε.	*d*.	P_2.	*t*.	ε.	*d*.	P_2.
20°	36·1	1·2035	94·2	120°	21·9	1·1042	97·5

of the meniscus at each temperature. Dielectric constants and densities were measured, in the same oil-bath, at temperatures very close to the round figures given (mostly within a few tenths of a degree) and constant to ± 0·05°. The measured values were then plotted against the temperatures on a large scale and corrected where necessary to even 20° intervals, in the first place arithmetically, using the mean temperature coefficient at the points in question, and checked graphically. The values therefore have the significance of actual measurements rather than interpolations on a smoothed curve.

The solutions were made up individually by weight in small stoppered flasks of about 100 c.c. capacity.

Purification of Liquids.—Nitrobenzene. Starting with a fairly pure product, this was repeatedly fractionated and dried over pure phosphoric oxide, from which it was removed by distillation under reduced pressure. It froze at a constant temperature of 5·75°; $d_{4^\circ}^{25^\circ}$ 1·1985.

Diisoamyl. A commercial product labelled "pure" was shaken twice with "100%" sulphuric acid, washed, dried with phosphoric oxide which it did not then colour on standing, and fractionally distilled; b. p. 159·6—160·4°/767 mm.

p-*Xylene.* A pure commercial product was fractionated, dried over phosphoric oxide, and distilled; b. p. 138·5—138·8°/770 mm.; f. p. 12·9°.

A preliminary graphical estimate of the slopes of the P_2–$(\varepsilon - 1)/(\varepsilon + 2)$ lines, which were drawn to converge at a common point of 80 c.c. at $(\varepsilon - 1)/(\varepsilon + 2) = 1$, gave an average moment of $\mu = 4{\cdot}25$ (in Debye units; 10^{-18} e.s.u.), the individual moments varying from 4·30 to 4·19 (*Nature*, **1934**, **134**, 458). In this, rather more weight was attached to the measurements in the more concentrated solutions, in which the uncertainty in P_2 caused by errors in the measurement of the dielectric constant is much less, and which lie very close to straight lines.

Calculation of the equations to the lines by the method of least squares gives the results in Table II, leading to an average value of $\mu = 4{\cdot}24$, as calculated from the expression $\mu = 0{\cdot}01273\sqrt{P_\mu T}$. The slopes of the lines are very nearly inversely proportional to the absolute temperatures.

TABLE II.

$P_2 = A - P_\mu(\epsilon - 1)/(\epsilon + 2)$.

t.	*A*.	P_μ.	$A - P_\mu$.	μ.	*t*.	*A*.	P_μ.	$A - P_\mu$.	μ.
20°	469·0	386·4	82·6	4·28	80°	392·0	311·7	80·3	4·22
40	442·0	361·1	80·9	4·28	100	372·4	293·2	79·2	4·21
60	412·5	329·5	83·0	4·22	120	355·9	279·4	76·5	4·22
							Average	80·4	4·24

The average value, 4·24, is very close to the value (4·23*D*) obtained by Groves and Sugden (this vol., p. 1094) from measurements with nitrobenzene vapour. It may be observed that the variation in the intercept at $(\varepsilon - 1)/(\varepsilon + 2) = 1$, which is equal to $A - P_\mu$, is small. With the present experimental accuracy one cannot say whether this variation is real, or due to experimental error. The lines do not pass through the points corresponding to the polarisations of the pure liquid, which for 20° and 120° are marked by crosses in the fig. The slight divergence from linearity at the upper ends of the lines suggests that the equations to the lines may contain some small additional term. Moreover, the temperature variation of the intercepts of P_2 at $(\varepsilon - 1)/(\varepsilon + 2) = 0$, yields an improbably high value for the dipole moment, which theoretically should not be the case if the simple linear formula given held strictly.

According to the theory of Raman and Krishnan (*loc. cit.*), the relation between the polarisation and dielectric constant in the liquid state may be written

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3}\nu\left(\frac{a_1 + a_2 + a_3}{3} + \frac{\mu^2}{3kT}\right) + \frac{\varepsilon - 1}{\varepsilon + 2}\nu\left(\Psi + \frac{1}{3kT}\Theta\right)$$

in which ν is the number of particles per unit volume, a_1, a_2, a_3, are the moments induced in the molecule along three axes by unit electric field, Ψ and Θ involve the effect of the anisotropy of the liquid on the optical and dielectric polarisations respectively, and the other symbols have their usual significance. It will be seen that the first term on the right-hand side of this equation is identical with Debye's expression, whilst the second term vanishes at $(\varepsilon - 1)/(\varepsilon + 2) = 0$.

Goss (*loc. cit.*) has assumed that this equation applies also to solutions, and has calculated the moments of methyl chloride and chloroform by plotting P_2 against $(\varepsilon - 1)/(\varepsilon + 2)$ for the pure liquid and for the solute at infinite dilution in hexane or carbon disulphide at three temperatures, joining the points and applying the Debye equation, ${}_TP = P_{e+a} + B\mu^2/T$, to the intercepts at $(\varepsilon - 1)/(\varepsilon + 2) = 0$. For methyl chloride, a good agreement with the observed gas value is obtained, but for chloroform, a much higher moment is found, which Goss ascribes to a change in the valency angles in the direction of a closer approach of the chlorine atoms in the liquid state. This procedure implies that the intercept of P_2 at $(\varepsilon - 1)/(\varepsilon + 2) = 0$ gives, at different temperatures, either the actual gas value at each temperature or one which bears a constant difference from the latter. This does not appear to be the case with nitrobenzene, unless one makes the *ad hoc* assumption that the moment of nitrobenzene is actually greater in the liquid state, for which there is at present no evidence.

The average value of the dipole moment of nitrobenzene obtained in the present work, $\mu = 4{\cdot}24$, is about 7—8% greater than the commonly accepted values for this property in benzene solution. This also agrees with Müller's formula (see above), according to which all dipole-moment measurements in benzene at 25° must be multiplied by 1·067 (± 0·005) to bring them to the gas values.

These results, therefore, suggest a method of obtaining, to a fair approximation, the true dipole moment of a substance from measurements in solution. The method at present is empirical, and the extent of its applicability can only be tested when more data are available. It is not to be expected, however, that solutes which are highly associated, such as alcohols and carboxylic acids, will show a linear relationship between the solute and volume polarisations at ordinary temperatures.

Thanks are due to Messrs. Imperial Chemical Industries, Ltd., for a grant.

THE UNIVERSITY, MANCHESTER. [*Received, September 22nd,* 1934.]