62. *The Apparent Polarisations of Paraldehyde in Non-polar Solvents Measured at 10 and 25 cm.*

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Direct observation has verified that, where the common non-polar solvents of low (centipoise order) viscosity are concerned, the results of the preceding paper are not due to a spectrum of relaxation times reaching into the 300-m. region. Signs of dispersion of orientation polarisation may be seen between 25 and 10 cm., but this is credibly reconcilable with the simple Debye formula and accepted molecular dimensions. Solutions of paraldehyde in medicinal paraffin (viscosity *ca.* 0·2 poise) have also been investigated.

THE measurements recorded in this communication were made for precautionary reasons. The time, τ (seconds) of molecular relaxation in a dielectric is given by the well-known equation of Debye as $\tau = 4\pi\eta r^3/kT$, where η is the macro-viscosity (poises), r is the molecular radius (cm.), k is Boltzmann's constant ($1{\cdot}37 \times 10^{-16}$ ergs/degree), and T is the absolute temperature. If f represents the frequency (in c./s.) of the applied alternating field which corresponds to τ (through the relation $\tau = 1/2\pi f$) we have : $fr^3 = kT/8\pi^2\eta$. Now, the viscosities of the solvents used in the previous work range from 0·2 to 2·0 centipoises. At 25°, therefore, the product fr^3 should be between $2{\cdot}5 \times 10^{-13}$ and $2{\cdot}5 \times 10^{-14}$. Fig. 1 illustrates the consequent dependence of f upon r.

Assuming paraldehyde to be a liquid composed of close-packed spheres, r may be calculated as $0{\cdot}665V^{1/3} \times 10^{-8}$ cm. (V = molecular volume), *i.e.* (since $d_4^{25} = 0{\cdot}990$), 3·40 A. Its viscosity at 20° is 1·18 centipoises (Muchin, *Z. Elektrochem.*, 1913, **19**, 820). Accordingly, if this solute exists in the pure state or in dilute solution (of the type customarily used for dipole moment measurements), as single molecules, its orientation polarisation (${}_{\text{O}}P$) should remain constant until the applied frequency approaches 10^9 c.p.s., *i.e.*, a figure safely distant from that (10^6 c.p.s.) utilised in the preceding paper.

FIG. 1.

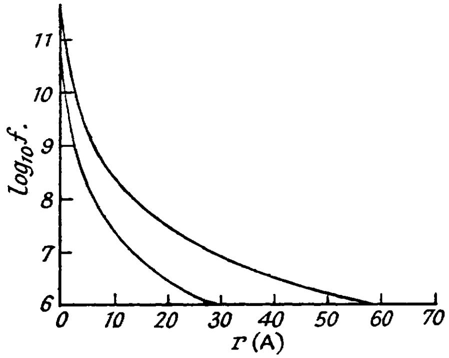
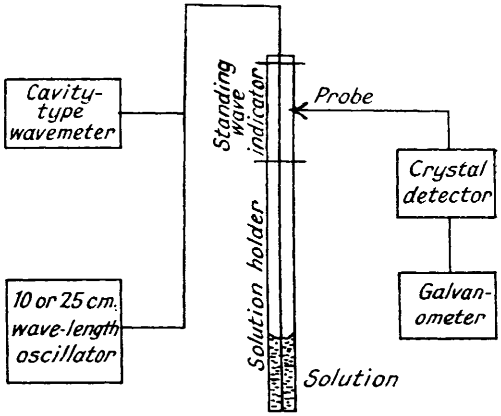


FIG. 2.



However, note should be taken of the following facts : the simple expression of Debye, implying spherical molecules freely rotating against one another and a single relaxation time, is too idealised. It indicates only the *order* of results obtained by direct experiment (cf. Holzmuller, *Physikal. Z.*, 1937, **38**, 574). Most molecules, in fact, would be more accurately regarded as ellipsoids with three axes, for which three values of τ should be foreseen *a priori* (Perrin, *J. Phys. Radium*, 1934, **5**, 497). In at least one instance (Girard and Abadie, *Faraday Soc. Discussion*, 1946, **42**, *A*, 40) dilution has revealed a plurality of dispersion regions. The coefficient of viscosity of flow is only a rough measure of the coefficient of internal friction really required by the Debye relation; for equal concentrations of the same solute in different solvents, maximum dielectric absorption does *not* occur at identical viscosities (Hall, Halliday, Johnson, and Walker, *ibid.*, p. 136). There are indications that the variations are connected with the shapes of the solvent molecules (Thompson, *ibid.*, p. 160). With benzophenone in benzene the incremental loss tangent is still diminishing as f descends past 10^8 c.p.s. (Jackson and Powles, *ibid.*, p. 106) ; with medicinal paraffin as solvent ($\eta = 1{\cdot}97$ poises) the corresponding point appears to be 10^6 c.p.s.—suggesting the presence of a spectrum of relaxation times.

Now, although cryoscopic studies (Paterno and Nasini, *Ber.*, 1886, **19**, 2529; Luginin and Dupont, *Bull. Soc. Chim.*, 1911, [iv], **9**, 223) in a few solvents have shown paraldehyde to be monomeric, there is still the possibility that in its dielectric behaviour it may act effectively either as double, treble, etc., units (through association, of the cybotactic type with itself) or as a lose structure carrying an " atmosphere " of solvent molecules. Were such to be the case a lower f should follow the greater r. In addition to other uncertainties already mentioned we cannot be sure that the variations of ${}_{\text{O}}P$ just reported have been of the kind we set out to study.

To delimit the possible existence of a similar " spectrum " with paraldehyde we have explored the effects of changing (*a*) the viscosity of the solvent or (*b*) the wave-length of measurement. In the following table we compare our results with those of the preceding paper :

Solvent.	Viscosity, poise.	Wave-length.	$({}_{\infty}P_1)_{25}$, c.c.
Light petroleum	*ca.* 0·003	*ca.* 300 m.	109
Medicinal paraffin	*ca.* 0·2	,,	124—125
Benzene	*ca.* 0·006	,,	117
,,	,,	25 cm.	113—124
,,	,,	10 cm.	102—107

The first two lines show that despite a 60—70-fold increase of viscosity, the total polarisation of paraldehyde is not diminished. It is similarly apparently unaffected by a change of measuring frequency from 10^6 c.p.s. (300 m.) to $1{\cdot}2 \times 10^9$ c.p.s. (25 cm.). The reduction recorded at $0{\cdot}3 \times 10^{10}$ c.p.s. (10 cm.) *may*, however, be real since (i) it appeared also at finite concentrations whenever the same solution was successively examined at the two shortest wave-lengths, and (ii) it leads to reasonable estimates for the relaxation time: if ${}_{\mathrm{T}}P_{\mathrm{obs.}} = 4\pi N[\alpha + \mu^2/3kT(1 + j\omega\tau)]/3$, then $j\omega\tau = ({}_{\mathrm{T}}P_{\mathrm{L}} - {}_{\mathrm{T}}P_{\mathrm{obs.}})/({}_{\mathrm{T}}P_{\mathrm{obs.}} - {}_{\mathrm{D}}P)$, where ${}_{\mathrm{T}}P_{\mathrm{obs.}}$ and ${}_{\mathrm{T}}P_{\mathrm{L}}$ are respectively the total polarisations observed at angular frequencies, ω, such that for the former $\omega\tau$ is not negligible, ${}_{\mathrm{D}}P$ is the distortion polarisation (44·5 c.c. for paraldehyde, cf. preceding paper), and τ is the relaxation time (defined as $\omega\tau = 1$). From our data at 300 m. and 10 cm. (above), $j\omega\tau$ lies between 0·16 and 0·26, whence $T_{25} = 8$—14×10^{-12} secs. That τ is of such an order seems possible from comparison with recorded values for other molecules, *e.g.*, camphor $6{\cdot}2 \times 10^{-12}$ secs. (in *cyclo*hexane at 30°; Whiffen, *J. Amer. Chem. Soc.*, 1948, **70**, 2452), chloroform $7{\cdot}7 \times 10^{-12}$ secs. (in benzene at $19° \pm 1°$; Jackson and Powles, *Trans. Faraday Soc.*, 1946, **42**, *A*, 101), or acetone $3{\cdot}2 \times 10^{-12}$ secs. (in benzene at $19° \pm 2°$; Whiffen and Thompson, *ibid.*, p. 118).

We conclude, therefore, that the variations of polarisation registered at 300 m. (preceding paper) are due to solvent influences and not to dispersion effects.

EXPERIMENTAL.

Measurements in Medicinal Paraffin.—The solvent was a commercial sample which had been stored over clean sodium wire for 2 days. It was used without further purification. Procedures followed our standard practice (cf. *J.*, 1948, 1949, and preceding papers, wherein the symbols used below are defined). Results are shown in the following table:

10^5w_1.	ε^{25}.	d_4^{25}.	P_1 (c.c.).	10^5w_1.	ε^{25}.	d^{25}.	P_1 (c.c.).
0	2·1467 *	0·8510	—	3964	2·2720	0·8543	121·3
2297	2·2193	0·8530	123·0	4435	2·2870	0·8549	121·5

* By direct comparison with benzene, $\varepsilon^{25} = 2{\cdot}2725$.

From these, the maximum and minimum values for $\alpha\varepsilon_2$ are 3·18 and 3·16, and for βd_2 0·0884 and 0·0845, whence ${}_{\infty}P_1 = 124$—125 c.c.

Measurements at 25 *and* 10 *cm.*—These have been made on co-axial equipment, the generators being a cavity tuned lighthouse triode oscillator and a reflex klystron respectively. A general outline of the apparatus is given in Fig. 2. Standard 5/8″ internal diameter, 51 ohm impedance transmission line was used for both the solution holder and the standing wave indicator (the latter was a U.S. War Dept. Type TS-56A/AP model).

The waves are propagated down the line, reflected up through the liquid from the short-circuited end, and the positions of voltage minima of the standing waves, with various depths of liquid in the line, are determined. By plotting the depth of liquid in the line against the distance of the minimum from the surface of the liquid, the wave-length in the liquid can be found. The apparent dielectric constant then follows as $(\lambda_{\mathrm{air}}/\lambda_{\mathrm{soln.}})$.

Since, in general, solutions were made up on different occasions and examined relatively to air—and not the pure solvent, as in ordinary dipole moment work—a separate determination of $\varepsilon_{C_6H_6}$ was also made in each case. Hence in the following table, the magnitudes of C $[= 3/d_2(\varepsilon_2 + 2)^2]$ and p_2 $[=(\varepsilon_2 - 1)/d_2(\varepsilon_2 + 2)]$ are not shown as the same for all solutions:

Paraldehyde in benzene.

	Wave-length = 10 cm.			Wave-length = 25 cm.		
10^5w_1	1029	3482	4765	1029	3482	4765
Temp.	23·0°	21·5°	21·3°	22·4°	22·0°	22·0°
d_4^t	0·8771	0·8813	0·8824	0·8774	0·8809	0·8815
$(p_2)^t$	0·3306	0·3389	0·3470	0·3305	0·3391	0·3378
C^t	0·1783	0·1875	0·1837	0·1918	0·1876	0·1882
$(\alpha\varepsilon_2)^t$	2·82	2·59	2·77	3·01	3·45	3·27
β^t	0·133	0·124	0·122	0·134	0·128	0·108
${}_{\infty}({}_{\mathrm{T}}P)^t$	104	103	108	114	125	121
${}_{\infty}({}_{\mathrm{T}}P)^{25}$	104	120	107	113	124	120

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