147. *The Dipole Moments of Liquids.*

By Frank R. Goss.

An investigation of the effect of the liquid state on the dipole moments of molecules (Müller, *Physikal. Z.*, 1933, **34**, 689) has made it evident that the several values which are obtained for any given compound fall into a regular order, which depends in the first place on the dielectric constant of the medium surrounding the substance under observation. In this paper the connexion between the polarisation coefficients of polar molecules and dielectric constants is considered from the standpoint of Raman and Krishnan's theory of electrical and optical properties. It has been shown (Goss, J., 1933, 1341) that this theory gives an exact explanation of the variation of polarisation and dielectric constant for a dipole-free substance, and the same theory is now applied to the calculation of the true dipole moments of liquids.

Other properties as well as the dielectric constant may affect the observed moment in special cases; *e.g.*, chemical reaction with the solvent in the case of the halogens (Müller and Sack, *Physikal. Z.*, 1930, **31**, 815), variation of the electronic structure of the molecule, as with hydrogen chloride (Stuart, *Z. Physik*, 1928, **51**, 497; Fairbrother, J., 1932, 43), and variation of the valency angles of particular atoms in the molecule, of which a good example is ethyl ether (Stuart, *loc. cit.*).

The relationship between polarisation and dielectric constant in the liquid state has been given by Raman and Krishnan (*Proc. Roy. Soc.*, 1928, *A*, **117**, 595) in an expression which may now be written as

$$P_2 = P_E + P_A + P_O + \frac{\varepsilon - 1}{\varepsilon + 2}N\psi + \frac{\varepsilon - 1}{\varepsilon + 2}\frac{N^2}{3RT}\Theta \quad . \quad . \quad . \quad . \quad (1)$$

where P_E, P_A, and P_O are the components of the polarisation for the gaseous state at the temperature T, ε is the dielectric constant of the liquid medium surrounding the molecule which has a polarisation P_2, N and R have their usual significance, and ψ and Θ involve the effect of the anisotropy of the medium on P_{E+A} and P_O respectively, as defined by Raman and Krishnan.

This expression (1) has already been applied to the special case where P_O and Θ are zero in a discussion of the polarisation coefficients of benzene by Krishnan (*ibid.*, 1929, *A*, **126**, 155) and by Goss (*loc. cit.*), and the validity of the expression for certain polar substances has been demonstrated by Sugden (*Nature*, 1934, **133**, 415), who has shown that for nitrobenzene, chlorobenzene, and benzonitrile, the relationship between P_2 and ε is of the form

$$P_2 = A + B\,(\varepsilon - 1)/(\varepsilon + 2)$$

The expression (1) shows that P_2 will be related to ε in this way unless it is also affected by other special properties such as those detailed in the second paragraph (above).

When $(\varepsilon - 1)/(\varepsilon + 2)$ is zero, $P_2 = P_E + P_A + P_O$, as in a gas. When $(\varepsilon - 1)/(\varepsilon + 2)$ is unity,

$$P_2 = P_E + P_A + P_O + N\psi + N^2\Theta/3RT \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Sugden has suggested (*loc. cit.*) that when $(\varepsilon - 1)/(\varepsilon + 2)$ is unity, then $P_2 = P_E + P_A$, but this condition is only realised in the above formula (2) if, after $N\psi$ has been neglected, a procedure which is often permissible, the relationship $4\pi\mu^2/3 = -\Theta$ can be said to hold. This condition is unlikely, and has not so far been found to exist except when μ is zero; indeed, it is evident that at the critical point Θ vanishes, while μ retains its usual value.

The expression (2) contains a number of coefficients which vary with temperature; P_2, P_O, ψ, and Θ all vary with the temperature T, and of these the variation of P_O is required to determine the true dipole moment given by $P_O = 4\pi N^2\mu^2/9RT$. The value of ψ can be readily obtained from refractivity measurements, and Θ can be calculated from the slope of the curve connecting P_2 with $(\varepsilon - 1)/(\varepsilon + 2)$, *i.e.*, from ${}_TK$ in the relation

$${}_TP = {}_TP_2 + {}_TK\,({}_T\varepsilon - 1)/({}_T\varepsilon + 2) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

To obtain the dipole moment of the substance, however, it is only necessary to obtain values of ${}_TP$ from the expression (3) for two or more values of T. In fact, it is necessary to measure at least two values of P_2 at two or more temperatures.

Typical examples of the numerous substances which obey the relationship (3) are the alkyl halides (Müller, *loc. cit.*). Accurate measurements have been made for methyl chloride as vapour by Sänger (*Helv. Phys. Acta*, 1930, **3**, 161), and as liquid by Morgan and Lowry (*J. Physical Chem.*, 1930, **34**, 2385). The data for methyl chloride as liquid and at infinite dilution in hexane are given below and plotted in the fig. The moment and the distortion polarisation, P_{E+A}, are calculated from the values of ${}_TP$, the Debye formula ${}_TP = P_{E+A} + B\mu^2/T$ being used.

Methyl Chloride.

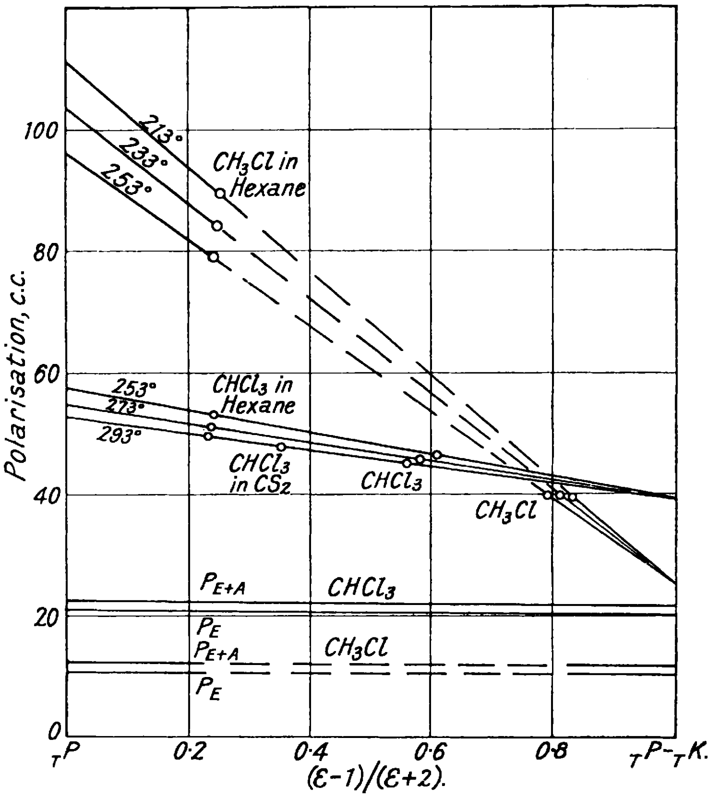
	In hexane.			As liquid.				
T.	P_∞.	ϵ.	$\frac{\epsilon - 1}{\epsilon + 2}$.	*P.*	ϵ.	$\frac{\epsilon - 1}{\epsilon + 2}$.	$_TP$.	$_TP - {}_TK$.
213°	89·3	2·020	0·2537	39·3	15·84	0·8318	111·2	24·7
233	84·0	1·992	0·2485	39·6	14·02	0·8127	103·6	24·9
253	79·0	1·965	0·2434	39·9	12·61	0·7947	96·2	25·5

$\mu = 1{\cdot}85$; * $P_{E+A} = 12{\cdot}6$ c.c.; $P_E = 11{\cdot}0$ c.c.

* Values of μ are given, here and throughout, in Debye units (e.s.u. × 10^{-18}).

The value for the moment given in this table may be compared with that of 1·56 for hexane solution, that of 1·71 obtained from the slope of the expression (3) (Sugden, *loc. cit.*) and finally, Sänger's value of 1·86 for the vapour.

Chloroform is another substance which in the liquid state obeys the relationship (3), as is evident from Müller's data (*loc. cit.*), and the moment has been calculated from Morgan and Lowry's data as in the case of methyl chloride. The results are given below and plotted in the fig., and in the latter is included the value of P_∞ for chloroform in carbon disulphide at 20° given by Müller (*loc. cit.*) in order to show that three values of P_2 at a given temperature are needed to make certain that the new method of calculating the moment is permissible.



Chloroform.

	In hexane.			As liquid.				
T.	P_∞.	ϵ.	$\frac{\epsilon - 1}{\epsilon + 2}$.	*P.*	ϵ.	$\frac{\epsilon - 1}{\epsilon + 2}$.	$_TP$.	$_TP - {}_TK$.
253°	53·1	1·965	0·2434	46·37	5·65	0·6078	57·6	39·2
273	51·1	1·938	0·2382	45·70	5·22	0·5845	54·8	39·2
293	49·7	1·910	0·2327	44·96	4·84	0·5614	53·0	38·6

$\mu = 1{\cdot}20$; $P_{E+A} = 22{\cdot}5$ c.c.; $P_E = 20{\cdot}9$ c.c.

The value for the moment of chloroform given in this table may be compared with that of 1·00 in hexane calculated by the usual method, and 0·95 for the vapour given by Sänger (*Physikal. Z.*, 1926, **27**, 556). The higher value for the moment in the liquid state would be accounted for if the angle between the chlorine atoms is less in the liquid state than in the vapour. Substances like methyl chloride, in which P_2 depends solely on ε, give a straight line which carries all values of P_2 as well as P for the vapour. Chloroform is a representative of those cases in which the dipole moment is different in the liquid and the vapour state, but in which the true moment of the liquid does not vary with the dielectric constant of the solvent, so that the values of P_2 still lie on a straight line.

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