29. *Studies in Dielectric Polarisation. Part XXI. The Effect of Solvent and Temperature upon the Polarisation and Apparent Moments of Bromides.*

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THE present paper, which describes measurements on bromobenzene and ethyl bromide, is a continuation of the work reported in Part XX (Cowley and Partington, J., 1936, 1184), in which the influences of the solvent and of the temperature in a particular solvent upon the moments of two nitriles were investigated. Determinations of the polarisations and apparent moments of bromobenzene and ethyl bromide have now been made over a temperature range in six solvents, *viz.*, hexane, *cyclo*hexane, carbon tetrachloride, benzene, toluene, and carbon disulphide. Since the moments of both these bromides have been accurately determined in the vapour state, we have compared vapour values calculated from solution data by the solvent-effect equations with the experimental results for the vapours. These calculations are mentioned in a later part of the paper.

The general conclusions from the present work resemble those deduced from the experiments on the nitriles. We find that all the values of the apparent moments of bromobenzene and ethyl bromide measured in solution are smaller than the vapour values for these compounds and that, within the limit of experimental error, the polarisation values for each compound found at any one temperature in the various solvents fall as the dielectric constant of the solvent increases.

The moments of the bromides have not previously been investigated in a number of solvents under the same conditions. The earlier results are given below :

Bromobenzene : vapour 1·71 (Groves and Sugden, J., 1935, 971) ; in hexane 1·60 at 25° (Hampson, *Trans. Faraday Soc.*, 1934, **30**, Appendix, p. 24) ; in carbon tetrachloride 1·53 (temperature method) (Das and Roy, *Indian J. Physics*, 1930, **5**, 441) ; in benzene 1·53 at 20° (Tiganik, *Z. physikal. Chem.*, 1931, *B*, **13**, 425), 1·70 (Daily, *Physical Rev.*, 1929, **34**, 548), 1·55 at 25° (Le Fèvre and Le Fèvre, J., 1936, 1130).

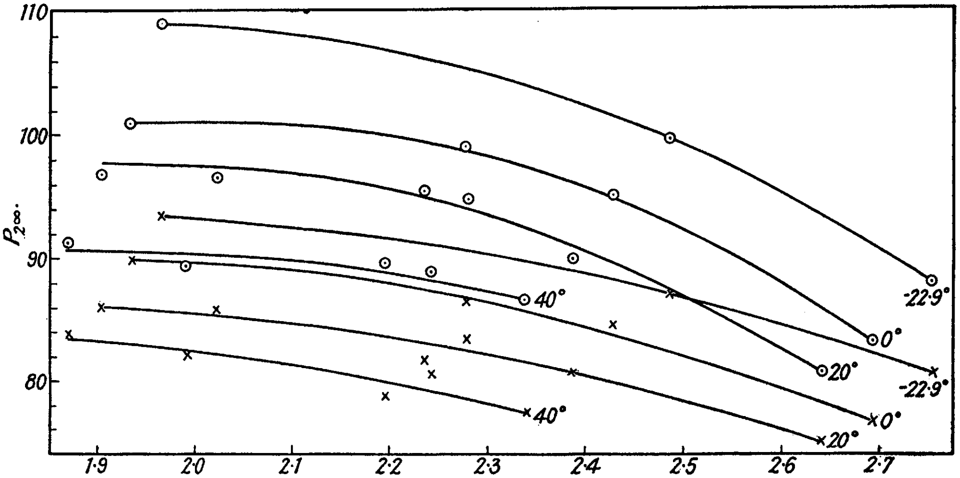
Ethyl bromide : vapour 2·02 (Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499), 1·99 (Mahanti, *Phil. Mag.*, 1935, **20**, 274) ; in hexane 1·86 (temperature method) (Smyth and Morgan, *J. Amer. Chem. Soc.*, 1928, **50**, 1547) ; in benzene 2·12 (Daily, *loc. cit.*). (The values of the moments are expressed here and throughout the paper in Debye units.)

The results of the present research are summarised in Table I, in which the temperature of measurement, $t°$; the solvent; the dielectric constant, ε, of the solvent; the polarisation of the solute at infinite dilution, $P_{2\infty}$; and the moment, μ, are given. As in the previous work, the moment has been calculated at each temperature from the difference of the total polarisation at infinite dilution and the electronic polarisation. These data may be compared with the results found in different solvents at 20° for the polarisations of chlorobenzene and *n*-propyl chloride (Müller, *Physikal. Z.*, 1933, **34**, 689) as these two compounds closely resemble the two bromides both in magnitude of moment and in molecular structure. The influence of the solvent on the polarisation is very similar for the two pairs of substances.

TABLE I.

Solute.		Bromobenzene : P_E = 34·0 c.c.			Ethyl bromide : P_E = 19·1 c.c.		
Temp. $t°$.	Solvent.	ϵ of solvt.	$P_{2\infty}$.	μ.	ϵ of solvt.	$P_{2\infty}$.	μ.
40°	C_6H_{14}	1·871	84·0	1·59	1·871	91·5	1·91
40	C_6H_{12}	1·990	82·2	1·56	1·990	89·5	1·89
40	CCl_4	2·197	78·8	1·50	2·196	89·7	1·89
40	C_6H_6	2·242	80·7	1·54	2·242	89·1	1·88
40	C_7H_8	2·339	77·5	1·48	2·338	86·8	1·84
20	C_6H_{14}	1·902	86·0	1·57	1·903	96·5	1·91
20	C_6H_{12}	2·020	86·0	1·57	2·021	96·5	1·91
20	CCl_4	2·237	81·7	1·50	2·236	95·6	1·90
20	C_6H_6	2·281	83·6	1·53	2·280	94·9	1·89
20	C_7H_8	2·386	80·8	1·49	2·385	90·0	1·83
20	CS_2	2·643	75·4	1·40	2·642	81·0	1·71
10	C_6H_{12}	2·035	87·5	1·56	2·037	98·0	1·90
10	C_6H_6	2·301	85·2	1·53	2·300	96·5	1·88
0	C_6H_{14}	1·933	90·0	1·57	1·933	101·0	1·90
0	CCl_4	2·276	86·5	1·52	2·277	99·3	1·88
0	C_7H_8	2·435	84·8	1·50	2·431	95·2	1·83
0	CS_2	2·697	77·0	1·38	2·695	85·6	1·71
−22·9	C_6H_{14}	1·966	93·5	1·55	1·965	109·0	1·90
−22·9	C_7H_8	2·488	87·2	1·47	2·485	100·0	1·81
−22·9	CS_2	2·758	81·0	1·38	2·755	89·5	1·69

The figures in Table I indicate that the moment decreases with increase of dielectric constant of the solvent at any one temperature and the polarisation values plotted against the dielectric constant show regular variations. This is the case at all the four temperatures at which several measurements have been made. The results are shown in the diagram. The variations found for the bromides are much smaller, as would be expected from the magnitude of the moments, than those found in the case of the nitriles; and the variation



The variation of $P_{2\infty}$ of bromobenzene (points indicated by X*) and ethyl bromide (points indicated by* ⊙*) with ϵ, the dielectric constant of the solvent, at various temperatures (given by the figures).*

of the moment in a particular solvent with the temperature, found for the latter compounds, is not evident here, as the moments of the bromides determined in one solvent remain constant within the limits of experimental error over the range investigated. The difference between the moments of two aromatic and aliphatic compounds of the same type in the vapour state can be compared with the difference from solution measurements. In the present instance, this difference for the vapours of ethyl bromide and bromobenzene is 0·30, whereas the difference between the moments of these two bromides under the same conditions from the above solution measurements is 0·31—0·40.

The lines obtained by plotting the values of the total polarisation at different temperatures in each solvent against the reciprocal of the absolute temperature are straight, the deviations of the readings lying within the error of measurement. Table II gives the values of the induced polarisation, P_{E+A}, obtained by extrapolation of these lines, and the value of the apparent atomic polarisation, P_A, is found by subtracting the electronic polarisation from the intercept.

TABLE II.

Solute.	Bromobenzene.		Ethyl bromide.		Solute.	Bromobenzene.		Ethyl bromide.	
Solvent.	P_{E+A}, c.c.	P_A, c.c.	P_{E+A}, c.c.	P_A, c.c.	Solvent.	P_{E+A}, c.c.	P_A, c.c.	P_{E+A}, c.c.	P_A, c.c.
C_6H_{14}	44	10	23	4	C_6H_6	40	6	25	6
C_6H_{12}	38	4	22	3	C_7H_8	40	6	28	9
CCl_4	37	3	27	8	CS_2	42	8	25	6

The average of these approximate values in Table II is about 6 c.c. for the apparent atomic polarisation of each of the bromides : both results are larger than the values deduced from the vapour measurements on these compounds. Smyth and McAlpine (*loc. cit.*), from measurements on ethyl bromide vapour, find P_A to be 2·9 c.c., which is considerably smaller than the earlier value found from solutions in hexane, *viz.*, 11 c.c. (Smyth and Morgan, *loc. cit.*). It has been pointed out (Smyth, *J. Chem. Physics*, 1933, **1**, 247; Smyth and McAlpine, *ibid.*, 1935, **3**, 347; Jenkins, *Trans. Faraday Soc.*, 1934, **30**, 739) that these high values of the atomic polarisation are due to the slope of the P_2–$1/T$ line, which is reduced by the change of the dielectric constant of the solvent with temperature, and thus makes the value of the intercept too large and the moment calculated from the slope too small. This is generally found to occur with the *n*-alkyl halides, so that the temperature method cannot be applied to these compounds with certainty. As explained above, we have calculated the moments at each temperature from ($P_{2\infty} - P_E$). Groves and Sugden (*loc. cit.*) take the value of the atomic polarisation of bromobenzene as 5% of P_E, *i.e.*, 1·7 c.c.

The variation of the polarisation with solvent and temperature has also been examined by Müller's method (*Physikal. Z.*, 1934, **35**, 346). When the values of $P_{O+A} \times T$, the product of the orientation polarisation and the absolute temperature of measurement, are plotted against those of ε, the dielectric constant of the solvent at the same temperature, a smooth curve results. The curvature is not very marked, as the variations with the dielectric constant are relatively small. The product $P_{O+A} \times T$ varies in the case of bromobenzene from $1{\cdot}56 \times 10^4$ in hexane at 313° abs. to $1{\cdot}18 \times 10^4$ in carbon disulphide at 250·1° abs., and for ethyl bromide from $2{\cdot}27 \times 10^4$ to $1{\cdot}76 \times 10^4$ under the same conditions.

It has already been mentioned that the moments of the vapours of bromobenzene and ethyl bromide are higher than the solution values. This might be expected for molecules which possess radicals on their dipole axes (Frank, *Proc. Roy. Soc.*, 1935, *A*, **152**, 171) and have positive Kerr constants (Higasi, *Bull. Inst. Phys. Chem. Res., Tokyo*, 1934, **13**, 1167).

Müller's equation (*Physikal. Z.*, 1933, **34**, 689) [see equation (1), Part XX, *loc. cit.*] is applicable to this type of molecule, and the results for the bromides at 20° have been corrected for the solvent effect by means of this equation. The calculated values of the total polarisation are given in Table III, together with that for the vapour at the same temperature. With the exception of the determinations in the anisotropic solvent carbon disulphide, the results are reasonably consistent and give average values of the total polarisation of 89·7 c.c. and 103·5 c.c. for bromobenzene and ethyl bromide, respectively. These correspond with moments of 1·60 and 1·99 respectively, whereas the experimental vapour values are 1·71 and 2·01. (The former two moments have been corrected for the atomic polarisation, on the assumption that P_A is 5% of P_E, so that the experimental vapour moments are comparable with the calculated values.) The agreement in the latter case is good, while in the former the calculated value is the smaller, but as the moment is somewhat smaller here, the same errors in the calculation would be relatively more serious. It may be noted that the results of solution measurements on chlorobenzene on correction by Müller's equation give values lower than that for the vapour of this compound. Thus, data in nine solvents give calculated vapour values of 1·62—1·67, with a mean value of 1·65, a little lower than the vapour value of 1·70 (McAlpine and Smyth, *J. Chem. Physics*, 1935, **3**, 55).

TABLE III.

Values of $P_{2\,\text{vapour}}$ calculated from the data at 20° by (*a*) Müller's and (*b*) Sugden's equation.

Solute.	Bromobenzene.		Ethyl bromide.	
Solvent.	(*a*).	(*b*).	(*a*).	(*b*).
C_6H_{14}	89·4	101·6	101·5	119·8
C_6H_{12}	90·4	103·7	103·1	122·8
CCl_4	87·9	101·4	105·5	127·1
C_6H_6	90·7	104·8	105·5	127·2
C_7H_8	88·9	102·4	101·9	122·7
CS_2	85·9	98·1	96·7	114·9
Mean (excepting value in CS_2)	89·7	102·8	103·5	123·9
Vapour value	97·6		106·4	

Calculations have also been made by using Sugden's equation (*Trans. Faraday Soc.*, 1934, **30**, 720) [see equation (2), Part XX] and the values so obtained are included in Table III. The variations between individual values calculated from results in different solvents are not large, with the exception of the values from carbon disulphide solutions. In the results of Table III no allowance has been made for the constant α of Sugden's equation. The mean values of the total polarisation of bromobenzene and ethyl bromide from Table III are 102·8 c.c. and 123·9 c.c. respectively. To make these values correspond with the vapour results of 97·6 c.c. and 106·4 c.c. respectively, the constant α would be about 5 c.c. for bromobenzene and 17 c.c. for ethyl bromide. These constants are only approximate, as they are mean values from determinations in a number of solvents.

In Part XX (*loc. cit.*) the equation (5), deduced by Govinda Rau (*Proc. Indian Acad. Sci.*, 1935, *A*, **1**, 498) from the theory of Raman and Krishnan (*Proc. Roy. Soc.*, 1928, *A*, **117**, 589) for a solution of a polar substance in a non-polar solvent, was applied to the results, and it was shown that the polarisation value corrected for solvent influences was, in the case of benzonitrile, nearly equal to that deduced from Müller's equation. We have used the equation in the present research, making assumptions for bromobenzene similar to those previously used for benzonitrile. The constants used for ethyl bromide and the solvents are taken from published data (Govinda Rau, *loc. cit.*; Krishnan and Rao, *Indian J. Physics*, 1929—30, **4**, 39; Ramanadham, *Proc. Indian Acad. Sci.*, 1934, *A*, **1**, 281) and are given in Table V. In the calculations, the values of the moments of bromobenzene and ethyl bromide are taken as 1·6 and 1·9 respectively. The calculated values are given in Table IV. (For definitions of the symbols in Tables IV and V, see Part XX, p. 1188.)

TABLE IV.

Solvent.	$P_{2\infty}$, c.c., soltn.	$-N\Psi_1\dfrac{3\alpha\epsilon_1}{(\epsilon_1+2)^2}$.	$-N\Psi_2\dfrac{\epsilon_1-1}{\epsilon_1+2}$.	$\dfrac{-N\Theta}{3kT}\cdot\dfrac{\epsilon_1-1}{\epsilon_1+2}$.	P_2, c.c., vapour.
		Bromobenzene : at 20°.			
C_6H_{14}	86·0	0·7	1·0	3·6	91·3
C_6H_{12}	86·0	0·8	1·1	3·9	91·8
CCl_4	81·7	0	1·3	4·5	87·5
C_6H_6	83·6	1·8	1·3	4·6	91·3
CS_2	75·4	1·0	1·6	5·5	81·5
		Ethyl bromide : at 20°.			
C_6H_{14}	96·5	0·4	0·4	3·4	100·7
C_6H_{12}	96·5	1·4	0·4	3·7	102·0
CCl_4	95·6	0	0·5	4·3	100·4
C_6H_6	94·9	2·6	0·5	4·4	102·4
CS_2	81·0	1·5	0·6	5·2	88·2

The average of the calculated values of the polarisation in the first four solvents for bromobenzene is 90·5 c.c., with a corresponding moment, corrected for P_A, of 1·61, while the experimental vapour value is 1·71. The most significant correction in the above calculations is the third term involving Θ (assumed equal to $\mu^2 s_1$). If it is assumed that the whole of the difference between the calculated and the experimental vapour polarisations is due to error in this term, a value of s_1 can be calculated from the vapour value of the polarisation. From the foregoing results for bromobenzene in hexane and benzene, s_1 is found to be about −2·5, of the same order as but larger than the value assumed in the calculations. Govinda Rau (*loc. cit.*) has already pointed out that the value of s_1 found in this way for some other compounds is larger than the figure deduced from theoretical considerations and used in the calculations. It seems, therefore, that in several cases the calculated value of the term $\mu^2 s_1$ is somewhat smaller than is necessary to account for its contribution to the difference between the solution and vapour values, a view in agreement with that expressed by Frank (*Chem. and Ind.*, 1936, **14**, 37). In view of the approximate nature of the treatment and the uncertainty in the constants involved in the calculations, the calculated and the experimental moments are reasonably close. The corresponding calculated values for the total vapour polarisation and moment corrected for P_A are 101·4 c.c. and 1·96 for ethyl bromide, whereas the experimental vapour moment is 2·01, in better agreement than in the case of bromobenzene.

TABLE V.

Solvent.	s_1.	s_2.	s_3.	$a_1 \times 10^{23}$.	$a_2 \times 10^{23}$.	$a_3 \times 10^{23}$.
C_6H_{14}	−1·78	0·89	0·89	1·44	1·07	1·07
C_6H_{12}	−0·75	−0·75	1·5	1·31	1·31	0·98
CCl_4	0	0	0	—	—	—
C_6H_6	−1·21	−1·21	2·42	1·41	1·41	0·71
CS_2	−0·91	0·46	0·46	1·43	0·59	0·59
C_6H_5Br	—	—	—	1·85	1·85	0·93
C_2H_5Br	−0·81	0·40	0·40	1·26	0·91	0·91

The method of Higasi (*Sci. Papers Inst. Phys. Chem. Res., Japan*, 1936, **28**, 284) can be used to find the relation between experimental and theoretical values of $\Sigma\mu_i/\mu$, where $\Sigma\mu_i$ is the sum of the induced moments produced by dissolving the molecule in a solvent, and μ is the dipole moment in the vapour state. The two compounds now being considered are somewhat similar in molecular structure to the two nitriles previously investigated, and fall into the same category as the latter compounds, having values of $k > 1$ and thus a negative value of A. [See equations (6)—(9); Part XX.] As no figures for k are available, the values of k assumed are: for bromobenzene 1·65 (Higasi, *loc. cit.*), and for ethyl bromide 1·3 (that of methyl bromide: the values for ethyl chloride and methyl chloride are approximately the same; cf. Stuart, "Molekülstructur," Berlin, 1934, pp. 221, 234). The calculated and experimental values of $\Sigma\mu_i/\mu$ are collected in Table VI, together with the necessary data for the solvents (all results relating to 20°). All the solution values of the moments in Table VI have been corrected for the atomic polarisation, taken as 5% of the electronic polarisation. The calculated values in the case of carbon disulphide, which are lower than the others, being omitted, the average values of the calculated vapour moments are 1·66 and 1·99 for bromobenzene and ethyl bromide respectively, compared with the experimental vapour values of 1·71 and 2·01.

TABLE VI.

Solute.		Bromobenzene (A = −0·112).				Ethyl bromide (A = −0·0673).			
			$\Sigma\mu_i/\mu$.				$\Sigma\mu_i/\mu$.		
Solvent.	$4\pi\nu a$.	μ, exptl.	Exptl.	Calc.	$\mu_{vap.}$, calc.	μ, exptl.	Exptl.	Calc.	$\mu_{vap.}$, calc.
(Vapour)	—	1·71	—	—	—	2·01	—	—	—
C_6H_{14}	0·693	1·54	−0·10	−0·08	1·68	1·90	−0·05	−0·05	2·00
C_6H_{12}	0·761	1·54	−0·10	−0·08	1·68	1·90	−0·05	−0·05	2·00
CCl_4	0·876	1·47	−0·14	−0·10	1·64	1·89	−0·06	−0·05	1·99
C_6H_6	0·898	1·50	−0·12	−0·10	1·67	1·88	−0·06	−0·06	2·00
C_7H_8	0·948	1·46	−0·14	−0·11	1·65	1·82	−0·09	−0·06	1·94
CS_2	1·062	1·37	−0·20	−0·12	1·58	1·70	−0·15	−0·07	1·84

The main uncertainty in the application of these last two theoretical formulæ is the evaluation of the difficultly accessible constants. In view of the approximations made to obtain these constants, the calculated figures for the vapour moments are on the whole in fairly satisfactory quantitative agreement with the experimental results.

EXPERIMENTAL.

The apparatus and technique employed in the present research have been described in preceding papers in this series (Cowley and Partington, J., 1935, 604; 1936, 1184).

Preparation of Materials.—*Bromides.* Bromobenzene (Kahlbaum) was purified by fractionating it twice through a column. The properties were: b. p. 155·0°/756 mm., $D_{4^\circ}^{20^\circ}$ 1·4950, $n_D^{20^\circ}$ 1·5600, $[R_L]_D^{20^\circ}$ 33·96 c.c. Figures for comparison are: b. p. 155·6°/760 mm. (Weger, *Annalen*, 1883, **221**, 71); 155·0°, corr. (Perkin, J., 1896, **69**, 1248); 154·6—155·0°/741·9 mm.; $D_{4^\circ}^{20^\circ}$ 1·4914, $n_D^{20^\circ}$ 1·5598 (Brühl, *Annalen*, 1880, **200**, 187); $D_{4^\circ}^{20^\circ}$ 1·4953 (Biron, *Chem. Zentr.*, 1910, **14**, I, 1912); b. p. 155·4—155·6°/760 mm., $D_{4^\circ}^{20^\circ}$ 1·4946, $n_D^{20^\circ}$ 1·5600 (Bugarsky, *Z. physikal. Chem.*, 1910, **71**, 712). Ethyl bromide (Kahlbaum) was twice shaken with concentrated sulphuric acid and separated. It was washed with distilled water several times, dried over calcium chloride, and twice fractionated. Its physical properties were: b. p. 38·2°/755 mm., $D_{4^\circ}^{20^\circ}$ 1·4600, $n_D^{20^\circ}$ 1·4244, $[R_L]_D^{20^\circ}$ 19·06 c.c. Previous determinations are: b. p. 38·4°/760 mm. (Timmermans, *Chem. Zentr.*, 1911, **15**, II, 1015; Tyrer, J., 1914, **105**, 2538), $D_{4^\circ}^{20^\circ}$ 1·45983 (Patterson and Thomson, J., 1908, **93**, 371), 1·4555, $n_D^{20^\circ}$ 1·42386 (Weegmann, *Z. physikal. Chem.*, 1888, **2**, 231), $D_{4^\circ}^{20^\circ}$ 1·4586 (Smyth and Morgan, *J. Amer. Chem. Soc.*, 1928, **50**, 1547), $n_D^{20^\circ}$ 1·4239 (I. C. T.).

Solvents. With the exception of hexane (" from petroleum "), which was obtained from Kahlbaum, the solvents were obtained from the same sources and were purified as described in Part XX (*loc cit.*).

Results.—The symbols and method of calculation are those previously employed in this series. The moments are calculated at each temperature from $P_{2\infty}$ minus P_E, P_A being included with the orientation polarisation. The solvent and temperature of each measurement are stated.

Solute: Bromobenzene.

In hexane at 40°.

f_2.	ϵ.	$D_{4^\circ}^{t^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·871	0·6566	29·52	—
0·014459	1·905	0·6666	30·31	83·7
0·027657	1·936	0·6755	31·02	83·6
0·039897	1·965	0·6839	31·66	83·0
0·053721	1·997	0·6935	32·35	82·2

$P_{2\infty} = 84·0$ c.c.; $P_E = 34·0$ c.c.;
$P_{2\infty} - P_E = 50·0$ c.c.; $\mu = 1·59$.

In hexane at 20°.

f_2.	ϵ.	$D_{4^\circ}^{t^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·902	0·6746	29·52	—
0·014459	1·938	0·6845	30·33	85·7
0·027657	1·972	0·6939	31·07	85·6
0·039897	2·003	0·7022	31·75	85·3
0·053721	2·039	0·7119	32·50	85·0

$P_{2\infty} = 86·0$ c.c.; $P_E = 34·0$ c.c.;
$P_{2\infty} - P_E = 52·0$ c.c.; $\mu = 1·57$.

In hexane at 0°.

f_2.	ϵ.	$D_{4^\circ}^{t^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·933	0·6925	29·51	—
0·014459	1·973	0·7026	30·38	89·6
0·027657	2·010	0·7119	31·17	89·6
0·039897	2·044	0·7204	31·88	89·0
0·053721	2·082	0·7303	32·65	87·9

$P_{2\infty} = 90·0$ c.c.; $P_E = 34·0$ c.c.;
$P_{2\infty} - P_E = 56·0$ c.c.; $\mu = 1·57$.

In hexane at −22·9°.

f_2.	ϵ.	$D_{4^\circ}^{t^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·966	0·7115	29·49	—
0·014459	2·010	0·7221	30·40	92·9
0·027657	2·052	0·7322	31·24	92·8
0·039897	2·090	0·7415	31·98	91·8
0·053721	2·133	0·7512	32·82	91·6

$P_{2\infty} = 93·5$ c.c.; $P_E = 34·0$ c.c.;
$P_{2\infty} - P_E = 59·5$ c.c.; $\mu = 1·55$.

In *cyclo*hexane at 40°.

f_2.	ϵ.	$D_{4^\circ}^{t^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·990	0·7596	27·48	—
0·010995	2·019	0·7670	28·07	81·5
0·021436	2·047	0·7741	28·64	81·4
0·032298	2·076	0·7813	29·22	81·3
0·041673	2·100	0·7878	29·68	80·4

$P_{2\infty} = 82·2$ c.c.; $P_E = 34·0$ c.c.;
$P_{2\infty} - P_E = 48·2$ c.c.; $\mu = 1·56$.

In *cyclo*hexane at 20°.

f_2.	ϵ.	$D_{4^\circ}^{t^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·020	0·7781	27·43	—
0·010995	2·052	0·7853	28·08	86·0
0·021436	2·082	0·7924	28·66	84·8
0·032298	2·114	0·8000	29·27	84·4
0·041673	2·141	0·8065	29·78	85·0

$P_{2\infty} = 86·0$ c.c.; $P_E = 34·0$ c.c.;
$P_{2\infty} - P_E = 52·0$ c.c.; $\mu = 1·57$.

In *cyclo*hexane at 10°.

f_2.	ϵ.	$D_{4^\circ}^{t^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·035	0·7874	27·41	—
0·010995	2·069	0·7950	28·07	87·4
0·021436	2·101	0·8023	28·67	86·3
0·032298	2·133	0·8099	29·27	85·2
0·041673	2·162	0·8165	29·81	85·0

$P_{2\infty} = 87·5$ c.c.; $P_E = 34·0$ c.c.;
$P_{2\infty} - P_E = 53·5$ c.c.; $\mu = 1·56$.

In carbon tetrachloride at 40°.

f_2.	ϵ.	$D_{4^\circ}^{t^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·197	1·5557	28·21	—
0·009065	2·223	1·5550	28·66	78·2
0·020477	2·257	1·5544	29·23	78·4
0·030396	2·288	1·5537	29·75	79·1
0·039254	2·314	1·5530	30·20	78·9

$P_{2\infty} = 78·8$ c.c.; $P_E = 34·0$ c.c.;
$P_{2\infty} - P_E = 44·8$ c.c.; $\mu = 1·50$.

In carbon tetrachloride at 20°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·237	1·5940	28·18	—
0·009065	2·266	1·5932	28·66	81·6
0·020477	2·303	1·5919	29·27	81·7
0·030396	2·335	1·5908	29·80	81·5
0·039254	2·365	1·5902	30·28	81·7

$P_{2\infty}$ = 81·7 c.c.; P_{E} = 34·0 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 47·7 c.c.; μ = 1·50.

In benzene at 40°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·242	0·8577	26·65	—
0·010889	2·278	0·8656	27·24	80·7
0·020779	2·310	0·8729	27·76	79·9
0·031199	2·344	0·8802	28·31	79·7
0·040406	2·375	0·8866	28·81	80·0

$P_{2\infty}$ = 80·7 c.c.; P_{E} = 34·0 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 46·7 c.c.; μ = 1·54.

In benzene at 10°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·301	0·8893	26·56	—
0·010889	2·342	0·8973	27·19	84·6
0·020779	2·380	0·9046	27·77	84·7
0·031199	2·419	0·9122	28·35	84·1
0·040406	2·454	0·9190	28·87	83·8

$P_{2\infty}$ = 85·2 c.c.; P_{E} = 34·0 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 51·2 c.c.; μ = 1·53.

In toluene at 20°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·386	0·8662	33·60	—
0·011377	2·418	0·8730	34·13	80·5
0·022612	2·451	0·8801	34·66	80·3
0·033160	2·481	0·8864	35·14	80·1
0·043308	2·511	0·8929	35·60	79·9

$P_{2\infty}$ = 80·8 c.c.; P_{E} = 34·0 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 46·8 c.c.; μ = 1·49.

In toluene at −22·9°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·488	0·9058	33·71	—
0·011377	2·527	0·9127	34·31	86·5
0·022612	2·567	0·9197	34·91	86·6
0·033160	2·605	0·9262	35·47	86·7
0·043308	2·640	0·9327	35·96	85·7

$P_{2\infty}$ = 87·2 c.c.; P_{E} = 34·0 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 53·2 c.c.; μ = 1·47.

In carbon disulphide at 0°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·697	1·2929	21·27	—
0·011036	2·751	1·2969	21·89	77·0
0·021846	2·802	1·3009	22·47	76·2
0·030500	2·849	1·3044	22·98	76·0
0·042312	2·906	1·3090	23·61	76·5

$P_{2\infty}$ = 77·0 c.c.; P_{E} = 34·0 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 43·0 c.c.; μ = 1·38.

In carbon tetrachloride at 0°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·276	1·6326	28·11	—
0·009065	2·309	1·6320	28·64	86·4
0·020477	2·351	1·6309	29·30	86·0
0·030396	2·387	1·6296	29·86	85·8
0·039254	2·420	1·6290	30·36	85·4

$P_{2\infty}$ = 86·5 c.c.; P_{E} = 34·0 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 52·5 c.c.; μ = 1·52.

In benzene at 20°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·281	0·8787	26·59	—
0·010889	2·320	0·8866	27·20	83·2
0·020779	2·356	0·8938	27·76	83·2
0·031199	2·395	0·9010	28·37	83·1
0·040406	2·427	0·9078	28·86	82·7

$P_{2\infty}$ = 83·6 c.c.; P_{E} = 34·0 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 49·6 c.c.; μ = 1·53.

In toluene at 40°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·339	0·8478	33·52	—
0·011377	2·368	0·8548	34·01	76·9
0·022612	2·397	0·8616	34·50	76·9
0·033160	2·426	0·8680	34·98	77·6
0·043308	2·453	0·8746	35·41	77·1

$P_{2\infty}$ = 77·5 c.c.; P_{E} = 34·0 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 43·5 c.c.; μ = 1·48.

In toluene at 0°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·435	0·8846	33·69	—
0·011377	2·472	0·8918	34·27	84·5
0·022612	2·507	0·8988	34·82	83·7
0·033160	2·539	0·9056	35·37	84·3
0·043308	2·573	0·9115	35·82	82·8

$P_{2\infty}$ = 84·8 c.c.; P_{E} = 34·0 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 50·8 c.c.; μ = 1·50.

In carbon disulphide at 20°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·643	1·2633	21·32	—
0·011036	2·691	1·2672	21·91	74·8
0·021846	2·741	1·2716	22·50	75·0
0·030500	2·778	1·2746	22·95	74·5
0·042312	2·831	1·2791	23·57	74·5

$P_{2\infty}$ = 75·4 c.c.; P_{E} = 34·0 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 41·4 c.c.; μ = 1·40.

In carbon disulphide at −22·9°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·758	1·3247	21·23	—
0·011036	2·819	1·3286	21·88	80·0
0·021846	2·881	1·3326	22·53	80·5
0·030500	2·928	1·3359	23·01	79·7
0·042312	2·992	1·3405	23·68	79·1

$P_{2\infty}$ = 81·0 c.c.; P_{E} = 34·0 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 47·0 c.c.; μ = 1·38.

Solute : Ethyl bromide.

In hexane at 40°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·871	0·6568	29·51	—
0·010815	1·901	0·6612	30·18	91·2
0·021909	1·932	0·6658	30·85	90·5
0·031863	1·960	0·6700	31·43	89·9
0·040300	1·985	0·6736	31·94	89·8

$P_{2\infty}$ = 91·5 c.c.; P_{E} = 19·1 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 72·4 c.c.; μ = 1·91.

In hexane at 0°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·933	0·6925	29·51	—
0·010815	1·971	0·6976	30·28	101·0
0·021909	2·010	0·7029	31·05	99·8
0·031863	2·045	0·7073	31·73	99·3
0·040300	2·078	0·7115	32·34	99·8

$P_{2\infty}$ = 101·0 c.c.; P_{E} = 19·1 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 81·9 c.c.; μ = 1·90.

In hexane at 20°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·903	0·6748	29·54	—
0·010815	1·937	0·6796	30·26	96·1
0·021909	1·972	0·6844	30·98	95·4
0·031863	2·005	0·6890	31·64	95·6
0·040300	2·033	0·6930	32·17	95·0

$P_{2\infty}$ = 96·5 c.c.; P_{E} = 19·1 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 77·4 c.c.; μ = 1·91.

In hexane at −22·9°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·965	0·7133	29·39	—
0·010815	2·006	0·7175	30·24	107·6
0·021909	2·050	0·7232	31·06	105·7
0·031863	2·089	0·7279	31·79	104·6
0·040300	2·124	0·7324	32·40	104·0

$P_{2\infty}$ = 109·0 c.c.; P_{E} = 19·1 c.c.;
$P_{2\infty} - P_{\mathrm{E}}$ = 89·9 c.c.; μ = 1·90.

In *cyclo*hexane at 40°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·990	0·7596	27·48	—
0·011198	2·028	0·7649	28·16	88·4
0·022499	2·066	0·7694	28·85	88·6
0·033081	2·102	0·7740	29·49	88·1
0·044380	2·142	0·7793	30·15	87·8

$P_{2\infty}$ = 89·5 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 70·4 c.c.; μ = 1·89.

In *cyclo*hexane at 10°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·037	0·7876	27·44	—
0·011198	2·082	0·7926	28·23	97·7
0·022499	2·127	0·7976	28·99	96·5
0·033081	2·170	0·8026	29·70	95·8
0·044380	2·217	0·8076	30·46	95·4

$P_{2\infty}$ = 98·0 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 78·9 c.c.; μ = 1·90.

In carbon tetrachloride at 20°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·236	1·5941	28·16	—
0·011285	2·288	1·5932	28·91	94·5
0·020309	2·330	1·5923	29·50	94·1
0·032703	2·387	1·5911	30·27	92·7
0·043769	2·438	1·5901	30·95	91·9

$P_{2\infty}$ = 95·6 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 76·5 c.c.; μ = 1·90.

In benzene at 40°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·242	0·8577	26·65	—
0·010361	2·288	0·8625	27·30	89·1
0·020265	2·332	0·8673	27·90	88·3
0·029903	2·375	0·8720	28·47	87·5
0·039828	2·421	0·8767	29·10	88·0

$P_{2\infty}$ = 89·1 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 70·0 c.c.; μ = 1·88.

In benzene at 10°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·300	0·8891	26·55	—
0·010361	2·354	0·8940	27·27	96·2
0·020265	2·407	0·8990	27·95	95·7
0·029903	2·458	0·9039	28·58	94·7
0·039828	2·513	0·9089	29·25	94·4

$P_{2\infty}$ = 96·5 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 77·4 c.c.; μ = 1·88.

In toluene at 20°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·385	0·8664	33·57	—
0·011197	2·430	0·8710	34·20	89·7
0·022016	2·474	0·8757	34·78	88·7
0·032097	2·516	0·8801	35·33	88·4
0·042638	2·560	0·8845	35·89	88·1

$P_{2\infty}$ = 90·0 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 70·9 c.c.; μ = 1·83.

In toluene at −22·9°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·485	0·9058	33·65	—
0·011197	2·544	0·9119	34·38	98·6
0·022016	2·596	0·9163	35·04	96·4
0·032097	2·645	0·9203	35·64	95·6
0·042638	2·695	0·9250	36·22	93·4

$P_{2\infty}$ = 100·0 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 80·9 c.c.; μ = 1·81.

In carbon disulphide at 0°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·695	1·2925	21·26	—
0·011142	2·779	1·2955	21·98	85·6
0·021769	2·858	1·2978	22·65	84·8
0·032732	2·941	1·3005	23·32	84·1
0·042396	3·015	1·3027	23·91	83·7

$P_{2\infty}$ = 85·6 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 66·5 c.c.; μ = 1·71.

In *cyclo*hexane at 20°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·021	0·7783	27·45	—
0·011198	2·064	0·7833	28·21	95·8
0·022499	2·107	0·7884	28·95	94·6
0·033081	2·148	0·7936	29·63	93·4
0·044380	2·193	0·7985	30·37	93·3

$P_{2\infty}$ = 96·5 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 77·4 c.c.; μ = 1·91.

In carbon tetrachloride at 40°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·196	1·5556	28·19	—
0·011285	2·242	1·5549	28·88	88·7
0·020309	2·279	1·5542	29·41	88·1
0·032703	2·330	1·5529	30·13	87·6
0·043769	2·376	1·5522	30·77	87·0

$P_{2\infty}$ = 89·7 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 70·6 c.c.; μ = 1·89.

In carbon tetrachloride at 0°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·277	1·6327	28·13	—
0·011285	2·335	1·6319	28·94	99·4
0·020309	2·380	1·6310	29·54	97·5
0·032703	2·444	1·6298	30·37	96·7
0·043769	2·503	1·6293	31·11	96·2

$P_{2\infty}$ = 99·3 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 80·2 c.c.; μ = 1·88.

In benzene at 20°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·280	0·8787	26·57	—
0·010361	2·332	0·8838	27·28	94·3
0·020265	2·381	0·8884	27·93	93·3
0·029903	2·430	0·8933	28·55	92·6
0·039828	2·482	0·8983	29·19	92·3

$P_{2\infty}$ = 94·9 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 75·8 c.c.; μ = 1·89.

In toluene at 40°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·338	0·8480	33·49	—
0·011197	2·379	0·8527	34·07	85·8
0·022016	2·418	0·8570	34·62	85·1
0·032097	2·455	0·8612	35·12	84·4
0·042638	2·493	0·8657	35·62	83·4

$P_{2\infty}$ = 86·8 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 67·7 c.c.; μ = 1·84.

In toluene at 0°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·431	0·8848	33·61	—
0·011197	2·482	0·8897	34·29	94·6
0·022016	2·532	0·8944	34·94	94·1
0·032097	2·577	0·8988	35·50	92·6
0·042638	2·627	0·9034	36·12	92·5

$P_{2\infty}$ = 95·2 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 76·1 c.c.; μ = 1·83.

In carbon disulphide at 20°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·642	1·2632	21·33	—
0·011142	2·716	1·2657	21·99	80·6
0·021769	2·787	1·2681	22·62	80·6
0·032732	2·861	1·2705	23·26	80·4
0·042396	2·927	1·2728	23·82	80·0

$P_{2\infty}$ = 81·0 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 61·9 c.c.; μ = 1·71.

In carbon disulphide at −22·9°.

f_2.	ε.	$D^{t°}_{4°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·755	1·3260	21·19	—
0·011142	2·849	1·3301	21·93	87·7
0·021769	2·938	1·3335	22·62	86·7
0·032732	3·032	1·3365	23·33	86·5
0·042396	3·113	1·3394	23·92	85·6

$P_{2\infty}$ = 89·5 c.c.; P_E = 19·1 c.c.;
$P_{2\infty} - P_E$ = 70·4 c.c.; μ = 1·69.

SUMMARY.

The apparent moments and polarisations of bromobenzene and ethyl bromide in six solvents have been measured over a temperature range. It has been found that all the values of the moments in solution are lower than the vapour results and that the polarisation at each temperature decreases with increase of the dielectric constant of the solvent. The figures have been examined by the solvent-effect equations and it is concluded that the agreement between the calculated values and the experimental vapour determinations is on the whole fairly satisfactory.

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