372. *The Dipole Moments of Vapours. Part IV. Aliphatic Ethers and Amines. The Magnitude of Atomic Polarisation.*

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Measurements are recorded of the dipole moments of a number of aliphatic ethers and amines in the vapour state. For diethyl ether a large number of observations has been made over a temperature range of 190° and the results analysed by the method of least squares. It is found that the moment deduced from the slope of the P–$1/T$ curve is 1·18 D, and that the constant term in Debye's equation has a value which gives an atomic polarisation which is only 8% of the value of P_E measured for the sodium-D line.

For three other ethers and three aliphatic amines a smaller number of observations has been made and analysed in a similar manner. In general, it has been found that the moment deduced from the slope of the P–$1/T$ curve agrees with that calculated on the hypothesis that P_A is 5% of P_E.

IN the course of our work on the dipole moments of vapours we have now examined a number of aliphatic ethers and amines. The moments * calculated from our observations are compared with those found by Sänger, Steiger, and Gächter (*Helv. Physica Acta*, 1932, **5**, 200) in Table I.

TABLE I.

Substance.	μ (G. & S.).	μ (S. S. & G.).	P_{A+E}.	P_E.	P_{A+E}/P_E.
1. Dimethyl ether	1·28	1·29	15·4	13·3	1·16
2. Diethyl ether	1·18	1·10	27·6	22·5	1·17
3. Di-*n*-propyl ether	1·18	1·02	41·3	31·7	1·30
4. Di-*n*-butyl ether	1·18	—	—	—	—
5. Methylamine	1·32	1·23	13·4	10·3	1·30
6. Dimethylamine	1·02	0·96	17·4	15·1	1·15
7. Trimethylamine	0·65	0·60	21·5	19·4	1·11

It will be seen that the agreement is good for substances **1**, **6**, and **7**, but that there are notable discrepancies for substances **2**, **3**, and **5**. It should be noted that our values are calculated directly from the observed polarisation at each temperature on the assumption that P_A is 5% of P_E measured for the sodium-D line. Sänger, Steiger, and Gächter determined the constants for the linear relation between P and $1/T$ by the method of least squares and thus determined μ and P_{A+E} independently. The values found by these workers for P_{A+E} are compared with P_E in the last three columns of the table; all their values of the ratio P_{A+E}/P_E are higher than 1·05 and are particularly high for those substances in which our values of the dipole moment are greater than theirs.

The determination of P_{A+E} as the constant in the Debye equation involves a considerable extrapolation (to $1/T = 0$) and it is necessary to have a large number of observations over a wide range of temperatures in order to obtain an accurate value. We have therefore made a special study of diethyl ether involving 30 measurements of the polarisation over a temperature range of 188°. These observations are set out in Table II. In general, we

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* All moments are expressed in Debye units, e.s.u. × 10^{-18}.

have worked with pressures of the order of 200 mm., at which the vapour should very nearly obey the ideal gas laws. The polarisations calculated on the assumption that the density of the vapour is ideal are given in col. 3; to correct for small deviations from ideal behaviour the value of d_i/d (where d_i and d represent the ideal and the real densities of the vapour respectively) has been calculated from Berthelot's equation of state, *viz.*,

$$pv = \boldsymbol{R}T\left\{1 - 0{\cdot}0703\frac{T_c}{T}\cdot\frac{P_c}{P}\left(6\frac{T_c^2}{T^2} - 1\right)\right\}$$

$P_{\text{corr.}}$ is then obtained by multiplying P by d_i/d. It will be seen that the correction is small and can therefore be taken as substantially correct.

TABLE II.

Diethyl Ether.

T.	p, mm.	P.	d_i/d.	$P_{\text{corr.}}$.	$P_{\text{calc.}}$.	Δ.	μ_2.
288°	195	54·2	0·9875	53·5	53·1	+0·4	1·18
,,	242	54·0	0·9849	53·2	,,	+0·1	1·17
,,	128	53·8	0·9920	53·4	,,	+0·3	1·18
,,	153	54·0	0·9904	53·5	,,	+0·4	1·18
332	183	50·1	0·9927	49·7	49·2	+0·5	1·19
,,	142	49·5	0·9943	49·2	,,	±0·0	1·17
,,	167	49·1	0·9933	48·8	,,	−0·4	1·16
,,	129	48·7	0·9949	48·5	,,	−0·7	1·16
349·5	131	48·3	0·9956	48·1	47·9	+0·2	1·18
,,	143	48·2	0·9952	48·0	,,	+0·1	1·18
,,	199	48·3	0·9933	48·0	,,	+0·1	1·18
375	152	45·7	0·9960	45·5	46·2	−0·7	1·15
,,	201	46·5	0·9947	46·3	,,	+0·1	1·17
,,	146	45·9	0·9961	45·7	,,	−0·5	1·16
,,	147	45·7	0·9961	45·5	,,	−0·7	1·15
,,	165	46·3	0·9956	46·1	,,	−0·1	1·17
415	137	43·8	0·9974	43·7	44·1	−0·4	1·16
,,	172	44·4	0·9967	44·3	,,	+0·2	1·18
,,	202	44·1	0·9961	43·9	,,	−0·2	1·16
,,	144	44·2	0·9972	44·1	,,	±0·0	1·17
430	151	43·0	0·9974	42·9	43·2	−0·3	1·16
,,	221	44·0	0·9962	43·8	,,	+0·6	1·19
,,	155	43·3	0·9974	43·2	,,	±0·0	1·17
,,	159	43·4	0·9973	43·3	,,	+0·1	1·17
464	271	42·1	0·9964	42·0	41·8	+0·2	1·18
,,	237	42·1	0·9968	42·0	,,	+0·2	1·18
,,	211	42·0	0·9972	41·9	,,	+0·1	1·17
476	172	41·7	0·9979	41·6	41·3	+0·3	1·18
,,	252	41·5	0·9969	41·4	,,	+0·1	1·17
,,	185	41·8	0·9977	41·7	,,	+0·4	1·18
						Mean	1·17 ± 0·01

By applying the method of least squares to the data in Table II it was found that the values of the constants in the Debye equation were

$$P = 23{\cdot}2 \pm 0{\cdot}3 + (8620 \pm 100)/T \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The values of P calculated by this equation are given in col. 6, and the differences, Δ = obs. — calc., in col. 7. From these differences the probable errors quoted in the above equation were calculated. From the second term, $\mu = 1{\cdot}18 \pm 0{\cdot}01$; this is in excellent agreement with the mean value of μ calculated from each observation and quoted in the last column, in which P_{A+E} is taken as $1{\cdot}05P_E = 1{\cdot}05 \times 22{\cdot}5 = 23{\cdot}6$. This value is a little greater than the constant term in equation (1) but the difference makes no appreciable change in the calculation of the moment.

The smaller number of observations made on the other substances referred to in Table I have been treated in the same manner, and the results are summarised in Table III. Two values of μ are quoted; of these, μ_1 is derived from the slope calculated by the method of least squares, and μ_2 is the mean of the values calculated from each observation on the assumption that P_A is 5% of P_E. It will be seen that these two methods give substantially the same result.

TABLE III.

Substance.	No. of obsvns.	Temp. range.	Dipole moment. μ_1.	μ_2.	P_{A+E}.	P_E.	P_{A+E}/P_E.
Dimethyl ether	8	290—428°	1·29 ± 0·01	1·28 ± 0·01	13·4 ± 0·5	13·3	1·01 ± 0·04
Diethyl ether	30	288—476	1·18 ± 0·01	1·17 ± 0·01	23·2 ± 0·3	22·5	1·08 ± 0·01
Di-*n*-propyl ether ...	8	331—473	1·20 ± 0·01	1·18 ± 0·01	32·5 ± 0·4	31·7	1·02 ± 0·01
Di-*n*-butyl ether......	8	385—455	1·16 ± 0·03	1·18 ± 0·01	43·3 ± 1·0	40·8	1·06 ± 0·02
Methylamine	8	288—417	1·33 ± 0·01	1·32 ± 0·01	10·0 ± 0·6	10·3	0·97 ± 0·06
Dimethylamine	7	288—427	1·02 ± 0·01	1·02 ± 0·01	15·8 ± 0·4	15·1	1·05 ± 0·03
Trimethylamine	8	289—418	0·62 ± 0·01	0·65 ± 0·01	20·9 ± 0·2	19·4	1·08 ± 0·01
							Mean 1·04

Col. 6 gives the value of P_{A+E} obtained by the method of least squares, and this is compared with P_E in the last two columns. It will be seen that the ratio P_{A+E}/P_E is in general greater than unity, and that the use of 1·05 for this ratio is amply accurate for the calculation of dipole moments from the observed polarisations.

The differences between our results and those of Sänger, Steiger, and Gächter are probably due to the fact that these workers used higher pressures (600—850 mm. for ethyl ether) which approached the saturation pressure of the vapour. We have found with a number of substances that under such conditions the polarisation is abnormal but becomes practically independent of the pressure when this is less than half the saturation value. At constant density, which these workers used, the error due to this cause would diminish as the temperature increases, but a small error in the observed values of P at the lower temperatures would introduce a comparatively large error into the slope calculated from the Debye equation.

EXPERIMENTAL.

The polarisations were measured with the apparatus described in Part I (J., 1934, 1094). In the tables below, T is the absolute temperature, p the pressure of the vapour in mm. of mercury, P the measured polarisation in c.c., and μ the dipole moment deduced on the assumption that P_A is 5% of P_E. All the values given for P_E refer to the sodium-D line.

Dimethyl ether was prepared from pure methyl alcohol and sulphuric acid at 140°; the gas was washed with sodium hydroxide and water, and collected in concentrated sulphuric acid cooled in ice. This solution was slowly dropped into water in a flask kept cool by running water; the liberated ether, after passing through a reflux condenser cooled in ice-water, was condensed at −80°. It was finally distilled at a temperature a little below its b. p., −23°.

T.	p.	P.	μ.	T.	p.	P.	μ.	T.	p.	P.	μ.
290°	104	48·9	1·28	346°	140	43·9	1·30	428°	181	37·4	1·27
,,	96	49·1	1·28	,,	133	43·9	1·30	,,	168	37·3	1·27
,,	107	49·1	1·28					,,	158	37·7	1·29
										Mean	1·28

Diethyl ether was prepared from absolute alcohol and purified as usual. The specimen used had b. p. 34·6°/760 mm., $d_{4°}^{20°}$ 0·7142 (I.C.T. give $d_{4°}^{20°}$ 0·714). The experimental data for this substance are given in Table II.

Di-*n*-propyl ether was prepared from *n*-propyl alcohol. The specimen used had b. p. 88·8°/757 mm., $d_{4°}^{20°}$ 0·7468 (I.C.T. give 0·747); $P_E = 31·7$.

331	95	59·6	1·19	445	156	52·3	1·17	473	153	51·1	1·17
,,	90	59·1	1·18	,,	152	52·9	1·19	,,	191	51·5	1·18
,,	98	59·5	1·18	,,	172	52·5	1·18			Mean	1·18

Di-*n*-butyl ether, prepared from *n*-butyl alcohol, had b. p. 140·5°/757 mm., $d_{4°}^{20°}$ 0·7685; $P_E = 40·8$.

385	111	64·6	1·17	425	95	62·9	1·18	455	126	61·4	1·17
,,	107	65·3	1·18	,,	124	63·1	1·18	,,	136	61·7	1·18
					119	62·7	1·17	,,	120	61·8	1·18
										Mean	1·18

Methylamine. The hydrochloride was recrystallised several times from alcohol and was finally extracted with chloroform. The pure product melted at 226°. The base was liberated with concentrated potassium hydroxide, dried over lime, and condensed at $-80°$; $P_E = 10·3$.

T.	*p.*	*P.*	*μ.*	*T.*	*p.*	*P.*	*μ.*	*T.*	*p.*	*P.*	*μ.*
288°	203	48·3	1·32	328°	198	43·0	1·31	417°	354	36·5	1·32
,,	195	48·6	1·33	373	233	39·6	1·32	,,	269	36·3	1·31
328	191	42·9	1·31	,,	245	39·3	1·31			Mean	1·32

Dimethylamine. The base, liberated from the purified hydrochloride, was dried over lime and condensed at $-80°$. After redistillation it had b. p. 7·2°/758 mm., $d_{4^\circ}^{0^\circ}$ 0·681 (I.C.T. give 0·680); $P_E = 15·1$.

288	150	38·1	1·02	354	151	34·0	1·02	427	215	31·1	1·03
,,	113	38·0	1·02	,,	147	34·0	1·02	,,	191	30·5	1·01
				,,	169	33·8	1·02			Mean	1·02

Trimethylamine, purified in a similar manner, had b. p. 3·4°/755 mm.; $P_E = 19·4$.

289	265	29·5	0·65	355	391	27·8	0·65	418	244	26·6	0·65
,,	256	29·7	0·66	,,	423	28·0	0·66	,,	417	26·8	0·66
				,,	325	27·8	0·65	,,	345	26·7	0·65
										Mean	0·65

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