301. *Comparison of the True and the Apparent Dipole Moments of Dissolved Ethers.*

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New measurements together with data in the literature are used to provide ratios between the true and the apparent dipole moments of dimethyl, diethyl, di-*n*- and di-*iso*-propyl, and di-*n*-butyl ethers. The empirical relationships previously suggested for the " solvent effect " cannot be applied with certainty owing to molecular flexibility and consequent doubt concerning the molecular shapes. The types of configuration which could lead to the μ_S^2/μ_g^2 values found by experiment are indicated.

In this paper we consider the applicability, to five simple aliphatic ethers, of the empirical equations advanced previously (cf. *J.*, 1950, 3370) to relate an apparent dipole moment of a dissolved substance to the true value as determined on the vapour. The present examples were originally selected because the first three members are known to possess Kerr constants which are algebraically negative (Stuart and Volkmann, *Ann. Physik*, 1933, **18**, 121):

	$10^{-15}K$ for λ = 5400 Å and press. = 760 mm.
Diemthyl ether	−5 at 18°
Diethyl ,,	−3·9 ,, 62·7°
Di-*n*-propyl ether	−2·3 ,, 123·9°

We have also added the cases of di*iso*propyl and di-*n*-butyl ethers, the Kerr effects for which have not yet been recorded, although for the former at any rate a markedly negative *K* may be presumed by analogy with di*iso*propyl ketone ($K = -15{\cdot}3 \times 10^{-15}$; Stuart and Volkmann, *loc. cit.*); this aspect is, however, less important now in view of results recently obtained here (cf. *J.*, 1950, 283, 290, 556, 3370).

Since the comparisons sought are those of the orientation polarisations as solutes to those as vapours, it is necessary to ascertain the total polarisations in the two states at one temperature as well as the Debye equations for each ether. Much of this information can be drawn from the literature.

Data providing Polarisations.—We list first (Table 1) a selection of measurements on ethers as gaseous dielectrics, with references in chronological order. Certain earlier and obviously approximate figures are omitted, *e.g.*, those calculated by Højendahl (Thesis, Copenhagen, 1928) from the work of Pohrt (*Ann. Physik*, 1913, **42**, 569). Where an author or combination of authors has made at various times redeterminations on the same substance, only the latest results are quoted, previous papers being noted in parentheses.

For each ether we have investigated the degree of concordance between the various authors by plotting their polarisation values against $1/T$. In the cases where only $(\varepsilon - 1)_T$ is given, the appropriate $(P)_T$ has been calculated. The Figure indicates that the agreement is better than might be expected from the Debye equations in Table 1.

By least squares, and from the data used in the Figure, we obtain the relations listed in Table 2. We suggest that this Table summarises the variation of *P* with *T* satisfactorily since inspection reveals that for the four homolgous *n*-alkyl ethers there are differences

TABLE 1. *Ethers as gases.*

Results given as	No. of temps.	References
Dimethyl ether		
$(\varepsilon - 1)_T$ values	3	Stuart, *Z. Physik*, 1928, **51**, 490.
$P = 15{\cdot}4 + 10{,}230/T$ ...	4	Sänger, Steiger, and Gächter, *Helv. Phys. Acta*, 1932, **5**, 20 1929, **2**, 130; 1930, **3**, 162).
$P = 15{\cdot}03 + 10{,}130/T$ ...	2	Ramaswamy, *Proc. Indian Acad. Sci.*, 1936, *A*, **4**, 108.
Total Pn.* at each temp.	3	Groves and Sugden, *J.*, 1937, 1779.
Diethyl ether		
$(\varepsilon - 1)_T$ values	4	Stuart, *loc. cit.*
,, ,, ...	3	Fuchs, *Z. Physik*, 1930, **63**, 824.
$P = 2{\cdot}76 + 7490/T$	4	Sänger, Steiger, and Gächter, *loc. cit.* (cf. also *Physikal. Z.*, 1927, **28**, 455; 1930, **31**, 306).
$P = 23{\cdot}2 + 8620/T$	8	Groves and Sugden, *loc. cit.*
Final μ only	—	Hobbs, Jacokes, and Gross, *Rev. Sci. Instr.*, 1940, **11**, 126.
Total Pn.* at each temp.	7	Moore and Hobbs, *J. Amer. Chem. Soc.*, 1949, **71**, 411.
*Di-*n*-propyl ether*		
$P = 41{\cdot}3 + 6350/T$	3	Sänger, Steiger, and Gächter, *loc. cit.*
Total Pn.* at each temp.	3	Groves and Sugden, *loc. cit.*
*Di*iso*propyl ether*		
$P = 38{\cdot}5 + 7717{\cdot}8/T$ ...	6	Present work.
*Di-*n*-butyl ether*		
Total Pn.* at each temp.	3	Groves and Sugden, *loc. cit.*

* Pn. = polarisation.

of $9{\cdot}2_5$, $10{\cdot}2_5$, and 8·6 c.c. between the successive distortion polarisations—amounts which compare reasonably with the refractivity increases (9·17 and 9·21 c.c., for the D line) from Et_2O to $Pr^n{}_2O$ to $Bu^n{}_2O$ (Vogel, *J.*, 1948, 616).

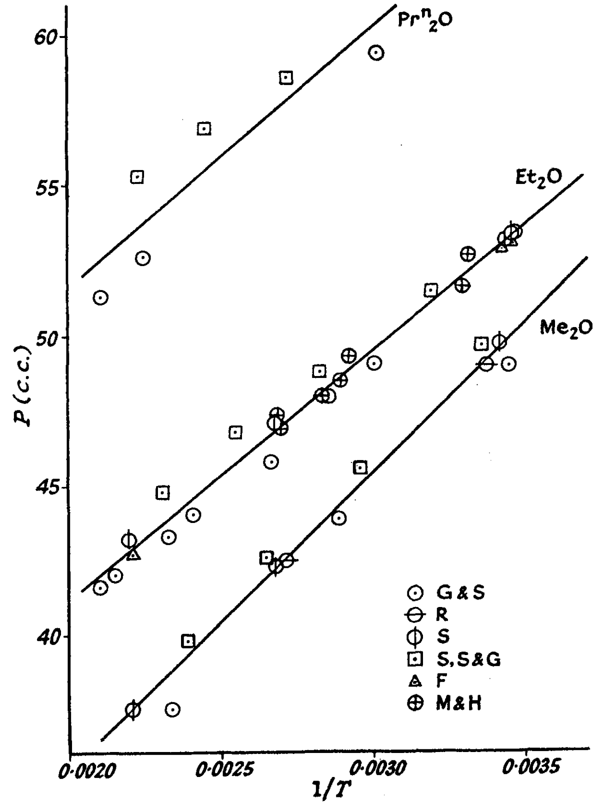


TABLE 2.

Me_2O	$(P)_T = 15{\cdot}2 + 10\,080/T$	$\mu = 1{\cdot}29$ D
Et_2O	$(P)_T = 24{\cdot}4_5 + 8340/T$	$\mu = 1{\cdot}17$ D
$Pr^n{}_2O$	$(P)_T = 34{\cdot}7 + 8505/T$	$\mu = 1{\cdot}18$ D
$Pr^i{}_2O$	$(P)_T = 38{\cdot}5 + 7718/T$	$\mu = 1{\cdot}13$ D
$Bu^n{}_2O$	$(P)_T = 43{\cdot}3 + 8303/T$	$\mu = 1{\cdot}16$ D

TABLE 3. *Ethers as solutes in benzene.*

Temp.	No. of solns. examined	Polarisation at infinite dilution (c.c.)	References
Dimethyl ether			
25°	6	47·3	Present work.
Diethyl ether			
20	5	54·8	Lange, *Z. Physik*, 1925, **33**, 169.
25	4	54·5	Williams and Krchma, *J. Amer. Chem. Soc.*, 1927, **49**, 1676.
18	10	56·9	Rolinski, *Physikal Z.*, 1928, **29**, 658.
18	3	57·0	Hassel and Uhl, *Z. physikal. Chem.*, 1930, *B*, **8**, 187 (cf. *Naturwiss.*, 1950, **18**, 247; *Z. Elektrochem.*, 1930, **36**, 735).
18·9	2	57·1	Meyer, *Z. physikal Chem.*, 1930, *B*, **8**, 27.
25	4	(56·6)	Spurr and Zeitlin, *J. Amer. Chem. Soc.*, 1950, **72**, 4832.
25	13	$56{\cdot}9_5$	Present work.
*Di-*n*-propyl ether*			
25	4	(66·8)	Spurr and Zeitlin, *loc. cit.*
25	8	60·8	Present work.
Diisopropyl ether			
25	5	71·3	Thomson, *J.*, 1937, 1056.
25	7	70·9	Present work.
*Di-*n*-butyl ether*			
25	11	74·5	Thomson, *loc. cit.*
25	4	71·7	Li and Pao-Chen Hsü, *J. Chinese Chem. Soc.*, 1926, **13**, 11.
25	4	(73·5)	Spurr and Zeitlin, *loc. cit.*

Table 3 presents measurements on the ethers when dissolved in benzene. The total polarisations are those shown by the authors cited, except in the cases of the Chinese paper (where we have deduced 71·7 c.c. from the dielectric constants and density figures given) and each of the results of Spurr and Zeitlin (where we have computed the polarisations from the μ and R quoted). Since with our own measurements we extrapolate the $(\varepsilon_{12} - \varepsilon_2)/w_1$ and $(d_{12} - d_2)/w_1$ values at each w_1 to $w_1 = 0$, we have re-examined the data of Thomson and of Spurr and Zeitlin in the same manner. For the former, with di*iso*propyl ether both $(\varepsilon_{12} - \varepsilon_2)/f_1$ and $(d_{12} - d_2)/f_1$ seem to be invariant with f_1, while with di-*n*-butyl ether this is true only of the density. Thus we find :

	Di*iso*propyl ether	Di-*n*-butyl ether
f_1 range	0 to 0·177	0 to 0·06
$(\alpha\epsilon_2)_{f_1}$	2·00	$1{\cdot}051 + 2{\cdot}2f_1$
$(\beta d_2)_{f_1}$	−0·0273	−0·2551

After adjustment to the basis where $\varepsilon^{25}_{C_6H_6} = 2{\cdot}2725$ and $d^{25}_{C_6H_6} = 0{\cdot}87378$, the coefficients at $f_1 = 0$ give—*via* Hedestrand's equation (*Z. physikal. Chem.*, 1929, *B*, **2**, 428)—total polarisations of 70·6 and 67·6 c.c. respectively for the dipropyl and the dibutyl ether. These results are somewhat lower than those listed by Thomson. Similar treatment of the f_1, ε, and d figures tabulated by Spurr and Zeitlin leads to abnormally high estimates of ${}_\infty P_1$ (*e.g.*, above 75 c.c. for diethyl ether). In Table 3 the polarisations quoted by the American authors for the three ethers concerned are inserted in parentheses.

Table 4 is included to show that the polarisations observed as dilute solutions in benzene, or as pure liquids, resemble one another closely. From the molecular volumes, V, and the distortion polarisations, ${}_DP$ (Table 2), $(n^{25}_{Eff})^2$ is obtained *via* $(n^{25}_{Eff})^2 = (V + 2\,{}_DP)/(V - {}_DP)$; for comparison the corresponding $(n^{25}_D)^2$ figures are also given (Table 4).

TABLE 4. *Ethers as liquids.*

	ε^{25}	d_4^{25}	${}_{T}P_{Liq.}$ (c.c.)	$(n_{Eff})^2$	$(n_D^{25})^2$
Et_2O	$4{\cdot}26_5$ [1]	0·708	54·5	2·218	2·086
$Pr^n{}_2O$	3·39 [2]	0·744	60·9	2·014	1·900
$Pr^i{}_2O$	4·04 [3]	0·720	71·4	2·117	1·863
$Bu^n{}_2O$	3·08 [3]	0·766	69·6	2·025	1·950

[1] Le Fèvre, *Trans. Faraday Soc.*, 1938, **34**, 1127. [2] Pyle, *Phys. Rev.*, 1931, ii, **38**, 1057. [3] Thomson, *loc. cit.*

TABLE 5.

	Me_2O	Et_2O	$Pr^n{}_2O$	$Pr^i{}_2O$	$Bu^n{}_2O$
$({}_{T}P)_{gas}$	49·0	$52{\cdot}4_5$	63·2	64·4	71·2
${}_{D}P$	15·2	$24{\cdot}4_5$	34·7	38·5	43·3
$({}_{O}P)_{gas}$	33·8	28·0	28·5	25·9	27·9
$({}_{T}P_{\infty})_{C_6H_6}$	47·3	$56{\cdot}9_5$	60·8	70·9	67·6
$({}_{O}P_{\infty})_{C_6H_6}$	32·1	32·5	26·1	32·4	24·3
μ_g	1·29	1·17	1·18	1·13	1·17
μ_s	1·25	1·26	1·13	1·26	1·09
${}_{O}P_s/{}_{O}P_g$	0·950	1·16	0·916	1·25	0·871

Discussion.—In Table 5 we assemble our results under the headings used before (Barclay and Le Fèvre, *J.*, 1950, 556; Angyal, Barclay, and Le Fèvre, *J.*, 1950, 3370).

The ratios forming the bottom line of Table 5 are now to be compared with figures calculated by equations (*a*), (*b*), and (*c*):

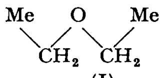
$$ {}_{O}P_s/{}_{O}P_g = 1 + k\,[\exp x^2 - (n^2_{Eff})_2/(n^2_{Eff})^2] \qquad (a) $$

$$ {}_{O}P_s/{}_{O}P_g = 1 + k\,[\exp x^2 - \exp (h_2{}^2 - h_1{}^2)] \qquad (b) $$

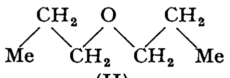
$$ {}_{O}P_s/{}_{O}P_g = 1 + k\,[\exp x^2 - \exp (R_1/R_2)\,(1 - A_1B_1C_1/A_2B_2C_2)] \qquad (c) $$

In these, subscripts 1 or 2 indicate solute or solvent respectively. For benzene at 25°, n^2_{Eff} is 2·300 (from measurements of ${}_{T}P_{gas}$ by McAlpine and Smyth, *J. Amer. Chem. Soc.*, 1933, **55**, 453, and Ramaswamy, *Proc. Indian Acad. Sci.*, 1936, *A*, **4**, 108), $(n_2{}^2)_D$ is 2·2417, the volume polarisation (k) is 0·2978 c.c., $[R_2]_D$ is 26·15 c.c., and $A_2B_2C_2$ is 117·6; requisite $[R]_D$ data for the ethers are taken from Vogel (*J.*, 1948, 616); Table 4 gives the relevant figures for $(n^2_{Eff})_1$ and $(n_1{}^2)_D$; x^2 and $h_1{}^2$ or $h_2{}^2$ are computed from diagrams incorporating "Wirkungsradien" as described in the papers cited at the head of this section ($h_2{}^2$ for benzene is 0·101).

As a basis for the construction of these scale drawings we have used the C–C and C–O interatomic distances and C–O–C angles listed by Allen and Sutton (*loc. cit.*) for dimethyl and diethyl ether. Only in the former case can the molecular shape be foreseen with certainty. For the higher homologues we initially tried an extended zig-zag arrangement (*e.g.*, as I and II), since *X*-ray analyses of long-chain solid aliphatic substances (cf., *e.g.*, Hendricks, *Chem. Reviews*, 1930, **7**, 431) suggested this as a reasonable first guess. However, Table 6 shows it to be unsatisfactory. Estimates, based on models of types such as (III), (IV), or (V), are therefore included for comparison. Good agreement with experiment is obtained if diethyl ether is given a "*trans*"-disposition of the two methyls about the C–O–C plane (indicated on edge by VI). For di*iso*propyl ether we have taken the H–C–O–C–H arrangement as flat, with the hydrogen atoms close together (*ca.* 1·7 Å between centres).



(I)



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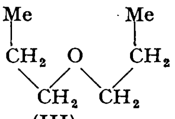

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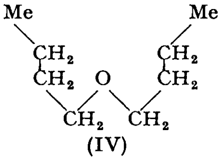

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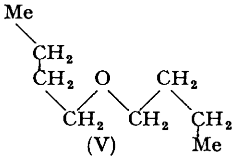
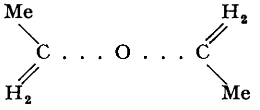


(V)



(VI)

However, while drawings indicate that these and other modifications are sterically allowable, we recognise the probability that, because of the flexibility of the alkyl radicals, the correct effective molecular shapes are some unknown average of all the possibilities. Such a suggestion is compatible with the information in Table 6, in which the various " calculated " ratios are compared with those " found."

We have pointed out in our previous papers that the usefulness of relation (*a*) for *a priori* computations of μ_{gas} is increased if accessible quantities such as n_D^2 may be employed in place of n^2_{Eff} (the evaluation of which implies preknowledge of polarisation–temperature measurements, from which μ_{gas} is directly available, for the gaseous substance). Accordingly we now list (Table 7) the " gas " dipole moments obtained *via* equation (*a*) from determinations with benzene as solvent, using n_D^2 figures from Table 4. It is seen that for each of four of the ethers a configuration (used last where more than one is considered) exists permitting an estimate of μ_{gas} within $\pm 3\%$ of the correct value. With the diethyl, di-*n*-propyl, and di-*n*-butyl members, the ratios $(n^2_{Eff})/(n_D^2)$ are all between 1·04 and 1·06 (cf. Table 4); for di*iso*propyl ether, however, the ratio is 1·14. If, in this instance, the " effective " refractive indexes are used, μ_{gas} is calculable as $1{\cdot}19_5$ D, and the error as 5·3—6·2%.

TABLE 6.

					${}_0P_s/{}_0P_g$ calc. *via* eqns.			${}_0P_s/{}_0P_g$ found
	A_1	B_1	C_1	R_1	(*a*)	(*b*)	(*c*)	
Me_2O	4·05	6·35	4·00	13·07 *	—	0·98	0·98	0·95
Et_2O (zig-zag)	4·42	8·80	4·00	22·51	0·98	1·00	1·06	1·16
,, (as VI)	4·36	7·20	6·90	,,	1·18	1·20	1·41	,,
$Pr^n{}_2O$ (zig-zag)	4·42	11·25	4·00	31·68	0·95	1·03	1·16	0·92
,, (as III)	5·95	7·90	4·00	,,	0·88	0·91	1·07	,,
$Pr^i{}_2O$	4·30	7·84	6·45	31·71	1·11	1·12	1·33	1·25
$Bu^n{}_2O$ (zig-zag)	4·42	13·85	4·00	40·89	0·95	1·06	1·24	0·87
,, (as IV)	6·81	10·37	4·00	,,	0·94	1·00	1·25	,,
,, (as V)	8·72	10·50	4·00	,,	0·83	0·95	1·16	,,

* Calc. from Vogel's atomic constants (*loc. cit.*). Lowery's measurements (*Proc. Phys. Soc.*, 1927, **40**, 27) on gaseous dimethyl ether lead to $R_{5461} = 13{\cdot}00$ c.c.

TABLE 7.

Ether	Me_2O	Et_2O	$Pr^n{}_2O$	$Pr^i{}_2O$	$Bu^n{}_2O$
$\mu_{C_6H_6}$	1·25	1·26	1·13	1·26	1·09
(μ_{gas}), calc.	1·26 *	1·28, 1·15	1·17, 1·21	1·23	1·12, 1·12, 1·20
(μ_{gas}), found	1·29	1·17	1·18	1·13	1·17
Error (%)	−2·3	+9·4, −1·7	−0·85, +2·5	+8·8	−4·3, −4·3, +2·6

* Equation (*b*) used, since n_D^2 not available at 25°. The configurations used for calculation of μ_{gas} are those listed in order downwards in Table 6.

EXPERIMENTAL

Materials, Apparatus, and Methods.—Dimethyl and di-*n*-propyl ethers were prepared from the corresponding alcohols, the former being scrubbed with potassium hydroxide solution and finally dried by passage through a potassium hydroxide tower. Other ethers were purchased. The liquid members were treated with sodium and fractionated immediately before use. The benzene was the frozen-out portion from " AnalaR " grade thiophen-free stock. It was stored over sodium wire. The dielectric constants of solutions have been determined with the apparatus noted previously (*J.*, 1948, 1949; 1949, 333); necessary data are tabulated below under the usual headings (cf. *Trans. Faraday Soc.*, 1950, **46**, 1, for definitions and explanation of extrapolation procedure adopted). For the measurements on gaseous di*iso*propyl ether we have used the circuit shown as Fig. 3 in *J.*, 1950, 276, together with the cell assembly illustrated in *J.*, 1950, 290. The third column of Table 8 reports polarisations computed relatively to carbon dioxide, whose polarisation is taken as invariant with temperature and equal to 7·341 c.c. (cf. *Trans. Faraday Soc.*, 1947, **43**, 374), by the expression :

$$P_{\text{Ether}} = 7{\cdot}341\ (\delta C/p)^{\text{Ether}}_{p=0}/(\delta C/p)^{CO_2}_{p=0}$$

The appropriate standardising equation was :

$$(\delta C/p)^{CO_2}_{p=0} = 2307{\cdot}4/T - 0{\cdot}054$$

TABLE 8. *Diisopropyl ether as a vapour.*

T (A)	$(\delta C/p)_{p \to 0}$	P (c.c.)	P (calc.)	p range (cm.)	No. of observations
354°	53·3	60·5	60·3	26—66	15
373	49·2	58·9	59·2	14—54	12
384	47·2	58·2	58·6	14—63	16
390	46·9	58·7	58·3	15—61	12
405	44·3	57·6	57·6	13—54	14
432	40·6	56·4	56·4	25—66	11

Whence (by least squares) $P = 38{\cdot}5 + 7717{\cdot}8/T$.

TABLE 9. *Solutions in benzene at* 25°.

$w_1 \times 10^5$	ε_{12}	$\alpha\varepsilon_2$	d_{12}	βd_2
0	2·2725	—	0·87378	—
		Dimethyl ether *		
1112	2·3084	3·23	0·87132	−0·221
2056	2·3387	3·23	0·86921	−0·222
2234	2·3477	3·37	0·86895	−0·216
2765	2·3675	3·44	0·86741	−0·230
4628	2·4364	3·54	0·86314	−0·230
5292	2·4543	3·44	0·86373	−0·190

Whence $(\alpha\varepsilon_2)w_1 = 3{\cdot}19 + 6{\cdot}28w_1$; mean $\beta d_2 = -0{\cdot}218$.

		Diethyl ether *		
11 617	2·2940	1·85	0·87159	−0·188
16 806	2·3047	1·98	0·87057	−0·191
21 118	2·3145	1·99	0·86983	−0·187
27 317	2·3232	1·86	0·86881	−0·182
30 123	2·3299	1·82	0·86821	−0·185
32 607	2·3315	1·81	0·86772	−0·186
34 537	2·3383	1·90	0·86720	−0·190
35 980	2·3413	1·91	0·86709	−0·186
37 168	2·3446	1·94	0·86703	−0·182
40 100	2·3470	1·86	0·86628	−0·187
44 178	2·3547	1·86	0·86565	−0·184
56 849	2·3781	1·86	0·86370	−0·177
128 050	2·5135	1·88	0·85010	−0·183

Whence mean $\alpha\varepsilon_2 = 1{\cdot}88$; mean $\beta d_2 = -0{\cdot}185$.

$w_1 \times 10^5$	ε_{12}	$\alpha\varepsilon_2$	d_{12}	βd_2
0	2·2725	—	0·87378	—
		Di-n-propyl ether		
715·2	2·2804	1·10	0·87266	−0·157
719·8	2·2803	1·08	0·87267	−0·154
1152	2·2844	1·03	0·87198	−0·156
1233	2·2862	1·11	0·87196	−0·148
1581	2·2889	1·04	0·87145	−0·147
2123	2·2952	1·06	0·87063	−0·148
2961	2·3043	1·07	0·86944	−0·147
3194	2·3085	1·13	0·86893	−0·152

Whence mean $\alpha\varepsilon_2 = 1{\cdot}08$; mean $\beta d_2 = -0{\cdot}151$.

		Diisopropyl ether		
1 364	2·2937	1·55	0·87168	−0·154
3 395	2·3254	1·56	0·86809	$-0{\cdot}167_5$
4 963	2·3499	1·56	0·86544	−0·168
8 554	2·4055	$1{\cdot}55_5$	0·85995	−0·162
12 668	2·4714	1·57	0·85388	−0·157
15 800	2·5237	1·59	0·84789	−0·164
20 077	2·5957	1·61	0·84188	−0·159

Whence $(\alpha\varepsilon_2)w_1 = 1{\cdot}54 + 0{\cdot}28w_1$; $\Sigma(d_{12} - d_2)/\Sigma w_1 = -0{\cdot}161$.

* The concns. in this case are $w_1 \times 10^6$.

The accuracies of the measurements on solutions may be gauged by applying the rule that the greatest probable error is $3\Sigma r/n\sqrt{n}$, where n is the number of observations made, and Σr is the sum of the differences (irrespective of sign) between the values of $\alpha\varepsilon_2$ and βd_2 from experiment and those obtained by averaging (or, where appropriate, by calculation). The polarisation at infinite dilution in benzene at 25° being given by $M_1p_2(1 - \beta) + M_1C\alpha\varepsilon_2$, the variations in $(1 - \beta)$ and $\alpha\varepsilon_2$, and hence the maximum error in $({}_TP_\infty)_{C_6H_6}$, may be set out as follows :

	Me_2O	Et_2O	$Pr^n{}_2O$	$Pr^i{}_2O$
$(1 - \beta)$	±0·014	±0·003	±0·004	±0·006
$\alpha\varepsilon_2$	±0·08	±0·04	±0·03	±0·01
Max. error in $({}_TP_\infty)_{C_6H_6}$ (c.c.)	0·9	0·6	0·7	0·4

Reference to Table 5 will show these as *ca.* 2, 1, 1, and 0·5% of the polarisations respectively. The higher uncertainty for dimethyl ether may be due to the difficulties of handling a gaseous solute.

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