173. *The Magnitude of the Solvent Effect in Dipole-moment Measurements. Part III. Polarisation and Association of Alcohols in the Liquid Phase.*

By Frank R. Goss.

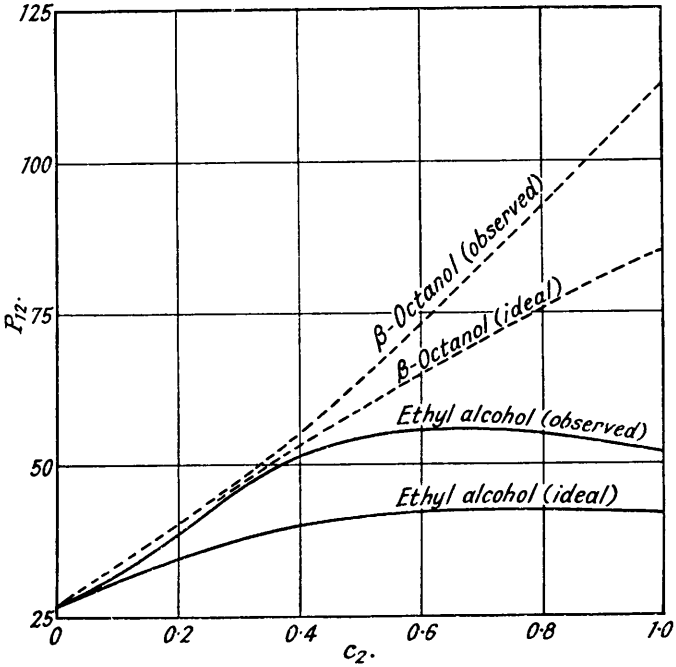
The dielectric polarisation of alcohols and their solutions is known to be highly abnormal, in agreement with the exceptional behaviour exhibited by their other physical properties such as vapour pressure, surface tension, and viscosity. The deviations of these liquids from the normal are commonly ascribed to some form of association, at one time thought to result in the formation of non-polar double molecules, but now shown to depend on the resonance of the molecules which may cause either an increase or a decrease in polarisation. On the basis of the solvent-effect equation introduced in Part I (J., 1937, 1915), and the correlated equations interrelating the polarisation constants developed there and elaborated in Part II (this vol., p. 752), it is now possible to calculate the ideal polarisation values which the alcohols would have if association could be eliminated. Consequently, the ratio of the observed partial orientation polarisation of alcohols in admixture with benzene to these ideal values is an association factor which indicates the incidence of the abnormal behaviour, in so far as polarisation is concerned. This factor is shown to vary, for the straight-chain alcohols, in close approximation to the $\frac{2}{3}$ power of the number of carbon atoms. The ideal dielectric constants of the unassociated alcohols are also calculated, and it is shown that in dilute benzene solution the alcohols behave normally, in agreement with cryoscopic observations. The pronounced minimum in the partial polarisation curve of the alcohols in admixture with carbon tetrachloride is discussed and is attributed to a heterogeneous association.

THE relationships established in Part II (*loc. cit.*) for the solvent effect are not directly applicable to associated liquids, such as those containing hydroxyl groups. Indeed, the deviation of the polarisation of alcohols in the liquid phase from normal behaviour has already been widely studied; it has been attributed to association by Debye (" Handbuch der Radiologie," 1925, **6**, 635) and specifically to certain types of molecular complexes by Wolf and Herold (*Z. physikal. Chem.*, 1934, *B*, **27**, 58; cf. Wolf, *Trans. Faraday Soc.*, 1937, **33**, 179). Thompson (J., 1938, 460) investigated mixtures of ethyl alcohol with certain ethers, and attributed the abnormal values of the polarisation to hydrogen-bond formation. These authors and also Hennings (*Z. physikal. Chem.*, 1935, *B*, **28**, 267) calculated the partial polarisation of the constituents of binary mixtures on the assumption that the value for one constituent was independent of concentration. The errors so introduced have been detailed in Part I (*loc. cit.*) on the basis of views put forward by Orr and Butler (*Nature*, 1932, **130**, 930). Nevertheless, even when the partial polarisations of alcohols are obtained by the intercept method, the values are still abnormal (cf. Coppock and Goss, J., 1939, 1789). In this paper an attempt is made to compare the abnormal curves found experimentally for the alcohols with calculated ideal curves. These can be obtained as in the case of normal, unassociated liquids if the polarisation of the liquid be derived from that of the vapour by correcting for the solvent effect alone (see Part II).

According to Sidgwick (*Ann. Reports*, 1934, **31**, 41), the homogeneous association of alcohols in the liquid phase involves the influence of an ionic state, which must materially change the polarisation. Moreover, the tendency for heterogeneous association with halogen (cf. Glasstone, *Trans. Faraday Soc.*, 1937, **33**, 200) will make benzene more suitable for investigating the polarisation than carbon tetrachloride, in spite of the advantages of the latter solvent which have been stressed in the earlier parts of this series. Stranathan (*Physical Rev.*, 1928, **31**, 653) has shown that the alcohols, when mixed with benzene, exhibit a normal polarisation at infinite dilution (P_∞), falling with rise in temperature. On the contrary, in carbon tetrachloride mixtures P_∞ rises with temperature. Smyth and Stoops (*J. Amer. Chem. Soc.*, 1929, **51**, 3312) have found a similar abnormal behaviour of P_∞ for alcohols in other solvents.

In this paper ideal curves for the partial polarisation of the unassociated alcohols are obtained by a method depending primarily on the fact that, so far as data are available, the experimental P_{12}-concentration curves (Fig. 1) for mixtures with benzene of the straight-chain alcohols and some of the branch-chain members consist (cf. Coppock and Goss, *loc. cit.*) of at least two portions; the dilute solution of the alcohol gives an entirely normal convex curve which, as shown later, can be attributed to unassociated alcohol molecules; the curve then passes for higher concentrations through a point of inflexion to a concave portion which is abnormal, and is due to the presence of the associated alcohol. The point of inflexion occurs at a molar concentration of 0·02 for ethyl alcohol, 0·03 for *n*-butyl alcohol, and 0·15 for β-octanol. These observations find a parallel in the case of cryoscopic measurements for ethyl alcohol in benzene, where Peterson and Rodebush (*J. Physical Chem.*, 1928, **32**, 709) record a normal molecular weight in dilute solutions ($c_2 < 0{\cdot}005$), in contrast to the rapid increase (cf. Fig. 4) found by Biltz (*Z. physikal. Chem.*, 1899, **29**, 249) with increasing concentration.

FIG. 1.



Polarisation–concentration curves for mixtures with benzene of ethyl alcohol and β-octanol at 20°.

The ideal polarisation curve should pass through the value which P_∞ for the carbon tetrachloride solutions would have if heterogeneous association between the liquids did not occur. The difference between the P_∞ values for benzene and carbon tetrachloride solutions is known to be close to 2 c.c. for a wide variety of normal polar components, especially in the case of those having moments of similar magnitude to the alcohols (some examples are given in Table I), and so it may reasonably be assumed that $P_\infty + 2$ for the benzene

TABLE I.

Effect on polarisation of varying the solvent.

	μ.	$P_\infty(CCl_4)$.	$P_\infty(C_6H_6)$.	Diff.
*iso*Propyl ether	1·22	76·0	74·0	2·0
Methylene chloride	1·54	70·0	68·0	2·0
Chlorobenzene	1·68	84·6	82·5	2·1
Bromobenzene	1·73	85·7	83·6	2·1
Ethyl bromide	1·94	98·0	94·9	3·1
Nitrobenzene	4·23	364·5	361·0	3·5

solutions lies on the ideal curve (see Fig. 2). The ideal curve of the partial polarisations (P_{S2}) plotted against $1/\varepsilon$ should also, by means of its intercepts Y and Z, be related to the orientation polarisation (P_O) of the vapour by the intercept ratio deduced in Parts I and II, *viz.*,

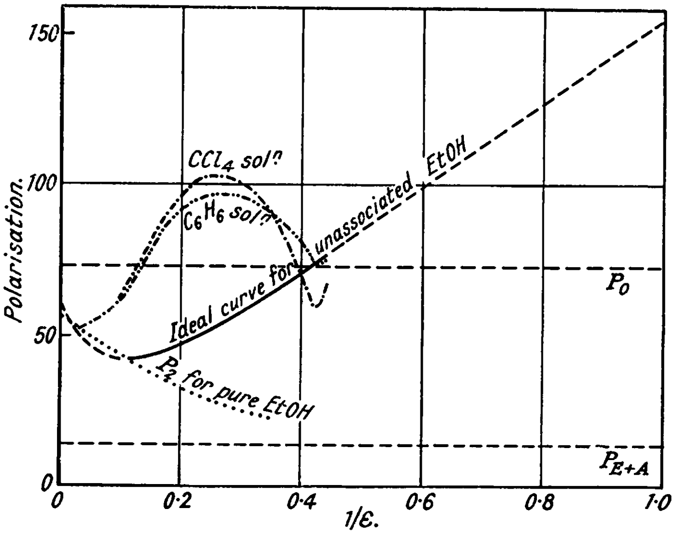
$$(Y/P_O - 1)/[\sqrt[4]{(Z + P_{E+A})/P_{E+A}} - 1] = 3 \quad . \; . \; . \; . \; . \quad (1)$$

This value of P_O can be obtained from the moments of methyl and ethyl alcohols in the vapour phase, which have been calculated with especial care by Stranathan (*J. Chem. Physics*, 1938, **6**, 395). The moment he obtained by taking $P_{E+A}/[R_L]_D$ as 1·05 (see Part II), corrected to the usual value of Avogadro's number for comparative purposes, was 1·68 D. for both alcohols. The value of the intercept Y can be obtained by application of the solvent-effect equation established in Part I, *viz.*,

$$P_{S2} = P_{E+A} + Z(\varepsilon - 1)^4/(\varepsilon + 2)^4 + Y/\varepsilon \quad . \; . \; . \; . \; . \quad (2)$$

for at infinite dilution $P_{S2} = P_\infty + 2 = P_{E+A} + Y/\varepsilon$ (the Z term has a very small value at this point; it is at first neglected and the appropriate corrections applied subsequently). Hence the value of the intercept Z can be calculated by the intercept ratio, and the ideal curve constructed by means of the solvent-effect equation.

FIG. 2.



Partial molar polarisations at 20° *of ethyl alcohol in mixtures with benzene and carbon tetrachloride.*

From these results it is possible to calculate the ratio of the electrical polarisation axes by the formula $K = 6{\cdot}55 - 3{\cdot}82\sqrt[4]{(Z + P_{E+A})/P_{E+A}}$ (see Part II). The value obtained for K in the case of both methyl and ethyl alcohol is less than unity, in agreement with the negative Kerr constants of the alcohols. This ratio K is, as shown in Part II, closely related to molecular structure. As far as the available evidence goes, for small values of K (as, *e.g.*, in the case of the ethers), it is independent of the length of the carbon chain. Hence, in order to proceed further and obtain the polarisation constants of the higher alcohols it will be assumed that they all have a K of the same value, 0·99. This means that Z/P_{E+A} is constant for the series of alcohols and hence that Z increases (see Table II) by a regular increment in the same way as P_{E+A}. Values of P_∞ for the benzene solutions have been carefully determined by the intercept method, data from the literature and also new determinations (see Table III and also Coppock and Goss, *loc. cit.*, Table III) being used.

TABLE II.

Polarisation constants of ideal solutions of alcohols at 20°.

	P_{E+A} = 1·05$[R_L]_D$.	*Z.*	*Y.*	P_O.	P_∞, in C_6H_6.	*K.*	μ, from (2).	μ, vapour.	*x.*	$\frac{1}{5}n^{\frac{2}{3}} + 1$.
Methyl alcohol	8·6	30	141	59·7	70	0·99	1 68	1·68	1·20	1·20
Ethyl alcohol	13·4	47	141	59·7	75	0·99	1·68	1·68	1·34	1·32
n-Butyl alcohol	23·2	81	141	59·7	85	0·99	1·68	1·66	1·50	1·50
α-Octanol	42·7	149	141	59·7	105	0·99	1·68	—	1·75	1·80
β-Octanol	42·7	149	132	55·9	101	0·99	1·63	—	1·64	—
β-Methylheptan-γ-ol	42·7	149	126	53·1	98	0·99	1·59	—	0·66	—

TABLE III.

Partial molar polarisations at 20°.

Methyl alcohol in benzene (Stranathan, *loc. cit.*, 1928; Akerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125); $[R_L]_D$ = 8·2; P_{E+A} = 8·6.

c_2.	P_{S2}.	P_{S1}.
0·00000	70	26·5
0·00890	69	26·5
0·01507	68	26·5
0·01929	68	26·6
0·02248	69	26·5
0·02929	71	26·4
0·03904	75	26·3
0·05278	81	26·0
0·06266	88	25·6
0·07135	92	25·3
1·00000	36·9	—

n-*Butyl alcohol in benzene* (Smyth and Stoops, *loc. cit.*); $[R_L]_D$ = 22·1; P_{E+A} = 23·2.

c_2.	P_{S2}.	P_{S1}.
0·0000	85	26·8
0·0211	83	26·8
0·0578	86	26·7
0·0798	89	26·4
0·1117	93	26·0
0·2525	106	22
0·4899	91	34
0·7385	80	50
1·0000	77·3	67

β-Methylheptan-γ-ol in benzene (Smyth and Stoops, *loc. cit.* p. 3330); $[R_L]_D$ = 40·7; P_{E+A} = 42·7.

c_2.	P_{S2}.	P_{S1}.
0·0000	98	26·8
0·0303	95	26·8
0·0331	95	26·8
0·0398	94	26·9
0·0502	93	26·9
0·0662	91	27·0
0·0889	89	27·1
0·2915	79	29
0·4892	74	32
0·6915	71	37
1·0000	69·6	45

Ethyl alcohol in benzene (see Table VI); $[R_L]_D$ = 12·8; P_{E+A} = 13·4.

c_2.	P_{S2}.	P_{S1}.
0·00000	75	26·6
0·00662	74	26·6
0·01156	73	26·6
0·01952	73	26·6
0·02674	75	26·5
0·03606	78	26·4
0·04942	80	26·3
0·07437	84	26·1
0·11115	89	25
0·17298	96	24
0·24867	96	24
0·33131	86	29
0·58705	60	49
0·81337	53	63
1·00000	51·9	71

Ethyl alcohol in carbon tetrachloride (see Table VI).

c_2.	P_{S2}.	P_{S1}.
0·00000	67	28·2
0·00765	65	28·2
0·01893	63	28·3
0·02928	60	28·3
0·04892	60	28·2
0·05718	62	28·1
0·08667	71	27
0·12075	84	26
0·15418	93	24
0·19044	99	23
0·22509	103	22
0·25809	103	22
0·28951	100	24
0·50833	66	46
0·71439	55	62
0·83864	53	70
1·00000	51·9	78

β-Octanol in carbon tetrachloride (see Table VI); $[R_L]_D$ = 40·7; P_{E+A} = 42·7.

c_2.	P_{S2}.	P_{S1}.
0·00000	96	28·2
0·00295	95	28·2
0·00624	94	28·3
0·00838	93	28·3
0·01783	91	28·3
0·03275	87	28·4
0·04718	83	28·6
0·09509	76	29
0·16199	80	28
0·23790	89	26
0·33406	97	23
0·61570	109	13
1·00000	111·9	0

Methyl alcohol in carbon tetrachloride (*loc. cit.*).

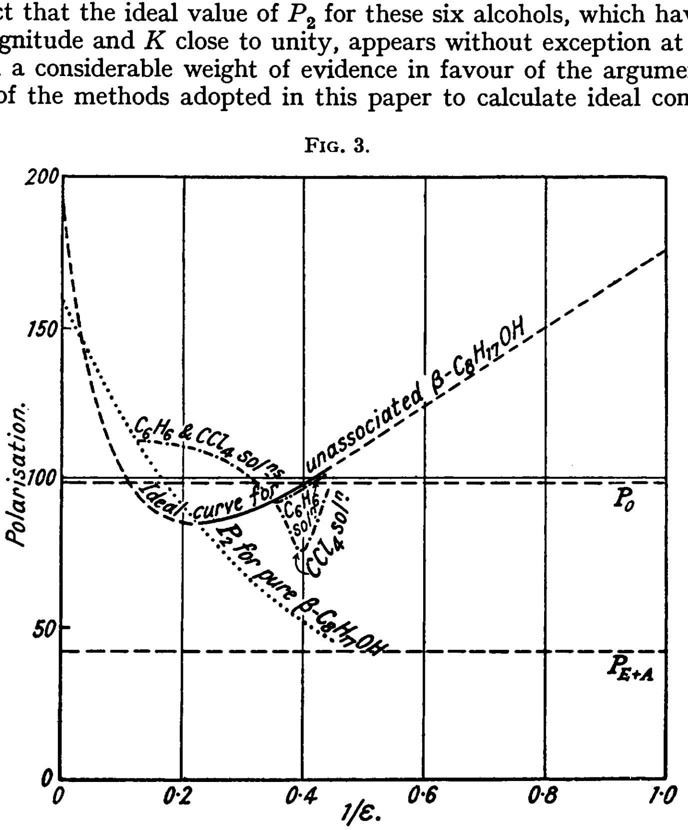
c_2.	P_{S2}.	P_{S1}.
0·00000	62	27·9
0·02219	57	27·9
0·02566	56	28·0
0·02819	55	28·0
0·03867	56	27·9
0·04358	57	27·8
0·05390	59	27·7
0·06162	61	27·6
0·07089	63	27·5
1·00000	36·9	—

α-Octanol in benzene (*loc. cit.*), $[R_L]_D$ = 40·7; P_{E+A} = 42·7.

c_2.	P_{S2}.	P_{S1}.
0·0000	105	26·8
0·0280	101	26·8
0·0406	100	26·8
0·0492	99	26·9
0·0666	98	27·0
0·0860	97	27·0
1·0000	119·4	—

Now a hypothetical curve can be drawn for the variation of the polarisation P_2 of the pure alcohol with a succession of arbitrary values assigned to its dielectric constant. In Figs. 2 and 3 such curves are plotted against 1/ε for ethyl alcohol and β-octanol respectively. It will be seen that two points on these curves are of significance, the experimental value of P_2 and the ideal value, where the hypothetical P_2–1/ε curve cuts the ideal P_{S2}–1/ε curve. Importance is attached to the fact that this intersection lies at the minimum point of the P_{S2}–$1/\varepsilon$ curves for all the alcohols discussed in this paper because the values of P_2 for the substances investigated in Parts I and II lie at, or very near, the minimum point, except where Y is very much greater than Z or where K differs considerably from unity. The fact that the ideal value of P_2 for these six alcohols, which have Y and Z of comparable magnitude and K close to unity, appears without exception at the minimum seems to afford a considerable weight of evidence in favour of the arguments now being advanced and of the methods adopted in this paper to calculate ideal constants for the alcohols. The ideal values of P_2 and ε are recorded in Table IV, together with the observed values for comparison. Further, the ideal value so obtained for the dielectric constant of *n*-butyl alcohol, *viz.*, 6·5, is related to that of the isomeric ether, 4·3, much as the value for ethylaniline, 5·9, is related to that of the isomeric tertiary amine, dimethylaniline, 4·5.

FIG. 3.



Partial molar polarisations at 20° of β-octanol in mixtures with benzene and carbon tetrachloride.

TABLE IV.

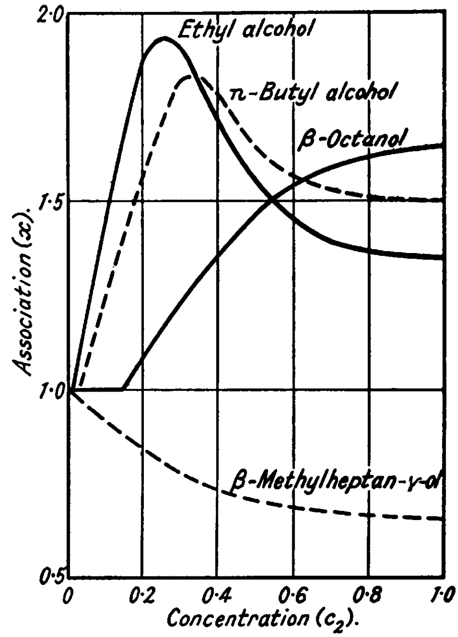
Ideal dielectric constants and polarisations of unassociated alcohols.

		P_2,		ε,	
	d.	ideal.	obs.	ideal.	obs.
Methyl alcohol	0·7918	31·8	36·9	12·0	32·3
Ethyl alcohol	0·7893	42·2	51·9	8·5	25·2
n-Butyl alcohol	0·8098	59·1	77·3	6·5	17·4
α-Octanol	0·8253	86·6	119·4	4·7	10·3
β-Octanol	0·8204	84·7	111·9	4·4	8·2
β-Methylheptan-γ-ol	0·8248	83·1	69·6	4·3	3·4

The ideal variation of the partial polarisation P_{S2} with $1/\varepsilon$ for the unassociated alcohols has thus been deduced and in the cases of ethyl alcohol and β-octanol is plotted in Figs. 2 and 3 respectively. The variation of P_{S1} for carbon tetrachloride with $1/\varepsilon$ is already known (see Part II, Fig. 3). Thus for any given value of $1/\varepsilon$, from the values corresponding to the pure alcohol to the value for the solvent, P_{S2} and P_{S1} are known, and by plotting the values as intercepts on the axes of a P_{12}–c_2 graph, tangents at a succession of points can be drawn and an ideal P_{12} curve for the unassociated alcohol constructed. Examples of these synthetic curves are given Fig. 1, where it will be seen that, above a certain value of c_2 characteristic of each alcohol, the observed polarisation is enhanced owing to the association. Now, this increase cannot be attributed in any way to P_E since the molecular refractivities of the alcohols show no abnormality and are indeed 0·4 c.c. lower than those of the isomeric ethers. It is unlikely that the large increase in polarisation which has to be accounted for could be due to an increase in the small value of P_A, particularly as P_E does not alter, so that it must be entirely due to an increase connected with P_O. Consequently, the association factor (x) can best be expressed as the ratio of the observed value of P_O for the alcohol to that obtained from the ideal curves at the same concentration. Values for the association expressed in this way are given for each pure alcohol in Table II and for some mixtures in Fig. 4. The more dilute solutions are normal, but above a certain critical concentration there is a rapid change in x. The values of x for the pure alcohols are directly proportional to the number of carbon atoms (n) in the case of the straight-chain members, being closely represented by the formula $x = \frac{1}{5}n^{\frac{3}{2}} + 1$ (see Table II). The variation of the association of the isomeric octanols with molecular structure has already been discussed by Smyth and Stoops (*loc. cit.*, p. 3330).

The curves for mixtures of carbon tetrachloride with ethyl alcohol and β-octanol, severally, have also been examined. Where these mixtures contain relatively large amounts of the alcohol, they bear a close resemblance to the corresponding benzene curves, but centred at $c_2 = 0{\cdot}04$ for ethyl alcohol and 0·10 for β-octanol, there occurs a sharp minimum, with the partial polarisation considerably lower (see Figs. 2 and 3) than with the benzene solutions. This is accompanied (see Table III) by a maximum in the polarisation of the carbon tetrachloride. In Hunter and Marriott's phraseology (this vol., p. 166), this may be attributed to heterogeneous association between the alcohol and the carbon tetrachloride partly superseding and partly coexisting with the homogeneous association of the alcohol. Association effects should decrease with rise in temperature and it is evident from the work of Stranathan (*loc. cit.*) that the difference in behaviour between the benzene and the carbon tetrachloride solutions tends to disappear at higher temperatures.

FIG. 4.



Association factors derived from polarisation data for alcohols in benzene solution.

EXPERIMENTAL.

Calibration of Condensers.—Density, dielectric constant, and temperature were measured as previously described (Goss, J., 1933, 1343; 1935, 730) except that the two experimental condensers of the Sayce–Briscoe type, which were used and silvered according to Sugden (J., 1933, 768), were calibrated * with reference to two liquids of known dielectric constant, on the assumption (cf. Ball, J., 1930, 583) that the change in capacity was directly proportional to the corresponding change in dielectric constant. This calibration was carried out with benzene and chloroform, recognised reference liquids (cf. Davies, *Phil. Mag.*, 1936, 21, 1), the dielectric constants of which were assumed to be 2·2825 and 4·806 respectively at 20° (see Table V). The condensers (II and III) had air capacities of 165 and 21 μμ F. respectively, and the accuracy of the calibration and of the linear relation assumed between the capacity of the condensers and the dielectric constants of the liquids was checked by measurements upon other reference liquids,

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* The dielectric constants recorded by Coppock and Goss (*loc. cit.*) were measured in these same condensers, calibrated as described in this paper.

TABLE V.

Values of ε for reference liquids at 20.°

	Condenser.		Recorded values.
	II.	III.	
Carbon tetrachloride	2·2411	2·245	2·242,[1] 2·236 [2]
Benzene	2·2825 *	2·282 *	2·2825 [3]
Chloroform	4·806 *	4·806 *	4·81,[4] 4·813,[5] 4·796,[2] 4·806 [6]
Chlorobenzene	5·706	5·68	5·685,[7] 5·714 [8]
β-Octanol	—	8·17	8·21 [11]
Acetone	—	20·96	21·17,[5] 21·40 [7]
Ethyl alcohol	—	25·23	25·0 [9]
Nitrobenzene	—	35·92	35·9,[4] 36·1 [10]

[1] Earp and Glasstone, J., 1935, 1709. [2] Davies, *loc. cit.* [3] Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 664. [4] Ball, J., 1930, 596. [5] Earp and Glasstone, J., 1935, 1720. [6] Goss, this vol., p. 752. [7] Ulich and Nespital, *Z. physikal. Chem.*, 1932, *B*, **16**, 221. [8] Davies, *Phil. Mag.*, 1936, **21**, 1008. [9] Akerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125. [10] Fairbrother, J., 1934, 1846. [11] Smyth and Stoops, *loc. cit.*, p. 3330. * Fixed points of scale.

the values found being in satisfactory agreement with those recorded in the literature as shown in Table V. The margin of error was estimated to range from ± 0·0005 for the lower values of ε to ± 0·01 for the higher values in the case of condenser II, and from ± 0·005 to ± 0·1 for condenser III.

Purification of Materials.—Carbon tetrachloride, benzene, and *dl*-β-octanol were purified as before (Goss, J., 1937, 1919; Coppock and Goss, *loc. cit.*). Absolute alcohol was refluxed with quicklime to $d_{4°}^{20°}$ 0·7897, corresponding to 99·9% of ethyl alcohol.

Results.—The experimental data, and the polarisations (P_{12}) for the binary mixtures calculated therefrom, are recorded in Table VI.

TABLE VI.

Polarisations at 20°.

c_2.	ε.	$d_{4°}^{20°}$.	P_{12}.	c_2.	ε.	$d_{4°}^{20°}$.	P_{12}.
			Ethyl alcohol and carbon tetrachloride.				
0·00000	2·2411	1·5941	28·24	0·19044	3·1924	1·4931	37·70
0·00765	2·2636	1·5905	28·51	0·22509	3·541	1·4735	40·33
0·01893	2·2970	1·5847	28·91	0·25809	4·023	1·4530	43·53
0·02928	2·3277	1·5794	29·27	0·28951	4·429	1·4347	45·59
0·04892	2·3764	1·5692	29·77	0·50833	9·094	1·2854	56·23
0·05718	2·4044	1·5651	30·09	0·71439	15·29	1·1103	57·20
0·08667	2·5069	1·5499	31·17	0·83864	19·35	0·9849	55·11
0·12075	2·6699	1·5326	32·86	1·00000	25·23	0·7893	51·92
0·15418	2·8926	1·5136	35·07				
			Ethyl alcohol and benzene.				
0·00000	2·2813	0·8790	26·60	0·11115	2·8444	0·8717	32·54
0·00662	2·3068	0·8785	26·89	0·17298	3·3640	0·8673	36·85
0·01156	2·3261	0·8782	27·12	0·24867	4·254	0·8625	42·29
0·01952	2·3544	0·8776	27·45	0·33131	5·620	0·8561	47·78
0·02674	2·3845	0·8772	27·79	0·58705	11·738	0·8361	55·41
0·03606	2·4309	0·8765	28·34	0·81337	18·92	0·8135	54·78
0·04942	2·4967	0·8757	29·07	1·00000	25·23	0·7893	51·92
0·07437	2·6196	0·8741	30·36				
			dl-β-*Octanol and carbon tetrachloride.*				
0·00000	2·2411	1·5941	28·24	0·09509	2·4550	1·4772	33·51
0·00295	2·2499	1·5900	28·44	0·16199	2·5823	1·4034	36·91
0·00624	2·2581	1·5858	28·63	0·23790	2·741	1·3270	41·01
0·00838	2·2711	1·5829	28·89	0·33406	3·049	1·2405	47·74
0·01783	2·2934	1·5707	29·42	0·61570	4·408	1·0314	71·81
0·03275	2·3286	1·5517	30·28	1·00000	8·173	0·8204	111·88
0·04718	2·3654	1·5338	31·14				

The author thanks Dr. J. Kenyon, F.R.S., for the loan of the specimen of racemic β-octanol, and the Chemical Society for a grant.

THE UNIVERSITY, LEEDS, 2.

[*Received, May* 21*st*, 1940.]