93.   *Solvent Effect in Dielectric Polarisation.   Part III.   The Behaviour of Ethyl Alcohol in Certain Ethers.*

By George Thomson.

The polarisation of ethyl alcohol has been measured in *iso*propyl, *n*-butyl, and amyl ethers and in dioxan. The high values of polarisation at infinite dilution and the variation of polarisation with concentration are explained by formation of a hydrogen bond between the ether and the alcohol. Evidence in support of this view is adduced from cryoscopic measurements in other ethers.

THE dielectric behaviour of the alcohols is of interest because, in non-polar solvents, the polarisation–concentration curves differ from those of other solutes in that they exhibit a maximum and not infrequently a minimum as well (cf., *inter alia*, Debye, " Handbuch der Radiologie," 1925, **6**, 635; Lange, *Z. Physik*, 1925, **33**, 169; Krchma and Williams, *J. Amer. Chem. Soc.*, 1927, **49**, 2408; Stranathan, *Physical Rev.*, 1928, **31**, 653; Smyth and Stoops, *J. Amer. Chem. Soc.*, 1929, **51**, 3312, 3330; Wolf and Herold, *Z. physikal. Chem.*, 1934, *B*, **27**, 58; Hoecker, *J. Chem. Physics*, 1936, **4**, 431).

In continuance of an investigation of the use of the aliphatic ethers as solvents in dielectric-polarisation measurements (Part I, J., 1937, 1051; Part II, *ibid.*, p. 1056), the polarisation of ethyl alcohol has been measured in di*iso*propyl, di-*n*-butyl, and diamyl ethers. The polarisation–concentration curves obtained are shown in Fig. 1, those for the last two solvents being of a different type from that in the first. High values are obtained in each case for the polarisation of the alcohol at infinite dilution: in *iso*propyl ether 91·9, in *n*-butyl ether 99·5, and in amyl ether 112. The polarisation of ethyl alcohol in the liquid state at 25° is 52·1 (Williams, *loc. cit.*), and in the vapour state at 25°, 72·4 (calculated from the data of Knowles, *J. Physical Chem.*, 1932, **36**, 2554). The exaltation of polarisation shown in solution in the ethers is too great to be accounted for simply by change in dielectric constant of solvent, and in any case is opposite in sign to the ordinary " solvent effect "; the alcohols are expected to show a polarisation increasing with increasing dielectric constant of the solvent (Higasi, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 284), though this effect is expected by Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171) to be small if, in fact, detectable. Hoecker (*loc. cit.*), working with extremely dilute solutions, found for ethyl alcohol at 24·5° in benzene $P_2 = 73·16 \pm 0·42$, and in carbon tetrachloride $P_2 = 71·31 \pm 0·33$. The value found by Knowles (*loc. cit.*) for the

vapour at this temperature was 72·8. There is general agreement that the shape of the polarisation curves for alcohols in non-polar solvents is due to association of the alcohol molecules, and Sidgwick (*Z. Elektrochem.*, 1928, **34**, 450) has suggested as the mechanism of association the formation of co-ordinate links between alcohol molecules, the oxygen of one molecule acting as donor and the hydroxylic hydrogen of another as acceptor. (For a modification of this in accordance with current theories, see Sidgwick, *Ann. Reports*, 1934, **31**, 41.) It seems probable that the behaviour of ethyl alcohol in the ethers is to be explained by the formation of a hydrogen bond between the ether and the alcohol R_2O .... HOR, the polarisation–concentration curves showing this effect superimposed on that due to co-ordination between the alcohol molecules. The latter effect should increase with increasing alcohol concentration, the former with increasing ether concentration. The capacity of the ethereal oxygen to form a hydrogen bond should be increased by the attachment to it of more strongly electron-repelling groups and would therefore be expected

FIG. 1.
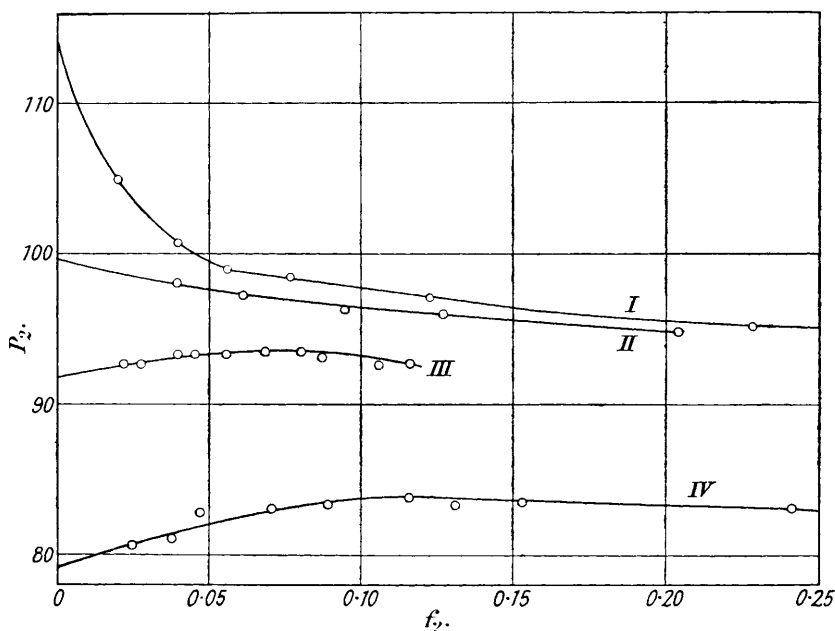
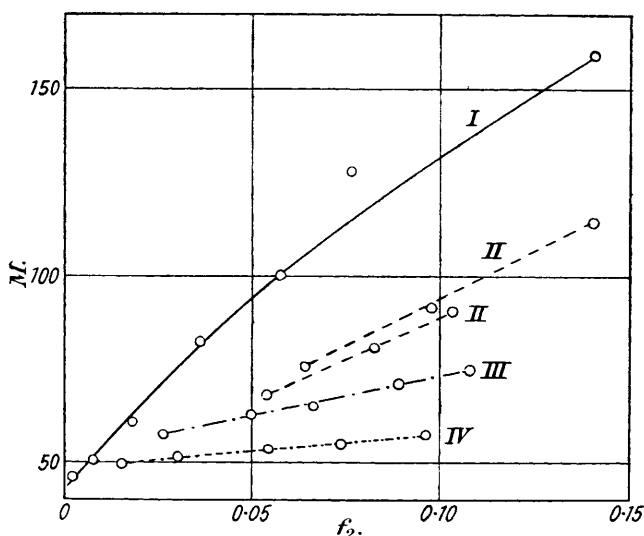*Ethyl alcohol in :* I, *amyl ether ;* II, *isobutyl ether ;* III, *isopropyl ether ;* IV, *dioxan.*

to increase with lengthening of the alkyl radical. Earp and Glasstone (*J.*, 1935, 1709) found that the formation of complexes with chloroform and bromoform proceeded more readily with *iso*propyl ether than with ethyl ether, and as a rough analogy the ionisation constants of the aliphatic secondary amines increase in the order diethylamine < *di*iso-propylamine < di-*n*-butylamine (Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469). No data are available for di-(β-methylbutyl)amine. (The amyl ether used seems to consist for the most part of the active ether.)

The propensity of dioxan to form molecular compounds is well known (cf. Rheinboldt and co-workers, *J. pr. Chem.*, 1931, **129**, 268, 273 ; 1932, **133**, 284), and Wilson and Wenzke (*J. Chem. Physics*, 1934, **2**, 546) have shown, from polarisation measurements, its efficacy in breaking down the dimers of acetic and propionic acids into simple molecules. Piperazine, the base corresponding to dioxan, has a lower dissociation constant than any of the aliphatic bases mentioned above, and it was therefore of interest to investigate the dielectric behaviour of ethyl alcohol in dioxan solution. The polarisation–concentration curve (Fig. 1) shows a maximum more pronounced than that obtained in *iso*propyl ether, and the value (79·2) of the polarisation at infinite dilution is lower.

Evidence from other physical properties for formation of a hydrogen bond is, in the case of these solutions, difficult to obtain. Smyth's view ("Dielectric Constant and Molecular Structure," 1931, p. 160), that such a link should result in an appreciable lowering in molecular refractivity, is negatived by the observation of Allard and Wenzke (*J. Amer. Chem. Soc.*, 1934, **56**, 1693) that the molecular refractivity of acetic acid is the same in solution in benzene and in dioxan. In the course of the present work, it was found that the molecular refractivity of ethyl alcohol in solution in butyl ether was indistinguishable from the value for the pure liquid.

Evidence from cryoscopic measurements seemed possible, for formation of a hydrogen bond between an alcohol and an ether molecule will tend to reduce the complexes which the alcohol molecules would otherwise form with one another and should therefore reduce the apparent molecular weights found by this method to values nearer that of the simple alcohol molecule. The effects of different ethers in this respect are shown in Fig. 2, which

FIG. 2.

Ethyl alcohol in : I, *benzene ;* II, *diphenyl ether ;* III, *ethyl cetyl ether ;* IV, *dioxan.*

presents the data obtained from cryoscopic measurements in diphenyl ether, ethyl cetyl ether, and dioxan. For comparison, the data obtained by Beckmann (*Z. physikal. Chem.*, 1888, **2**, 715) for ethyl alcohol in benzene solution are included. The rate of increase of apparent molecular weight with increasing ethyl alcohol concentration diminishes progressively through the series of solvents : benzene > diphenyl ether > ethyl cetyl ether > dioxan, the difference between diphenyl ether and dioxan being very marked. It must, however, be borne in mind that each molecule of dioxan can form links with two alcohol molecules, and moreover has such a low molecular weight that removal of dioxan as complex will be slow to show its effect. Ethyl cetyl ether has the disadvantage that, owing to its very high molecular weight, any complex formation with the solute will result in rather rapid removal of solvent and more rapid increase in apparent molecular weight of the solute.

EXPERIMENTAL.

Materials.—For methods of purification of ethers see Part I (*loc. cit.*). The diisopropyl ether had been subjected to prolonged drying over sodium, and the fraction used distilled at 68·4—68·5°/764 mm. It had $d_4^{20°}$ 0·72376, $d_4^{25°}$ 0·81849, $\varepsilon_{25°}$ 3·9511. The di-n-butyl ether had $d_4^{25°}$ 0·76569, $\varepsilon_{25°}$ 3·0806, and the diamyl ether $d_4^{25°}$ 0·77165, $\varepsilon_{25°}$ 2·8220. The dioxan was

1 : 4-dioxan " pure for molecular weight determinations," m. p. 12°, $d_4^{25°}$ 1·0272, $\epsilon_{25°}$ 2·2874. The ethyl alcohol was " absolute " alcohol freshly distilled from calcium oxide, b. p. 78·2°/758 mm., $n_D^{25°}$ 1·35956. The diphenyl ether had m. p. 27°. Ethyl cetyl ether was prepared by adding cetyl iodide (1 mol.) to sodium ethoxide (2 mols.) in ethyl alcohol, and warming the mixture on the water-bath for a few hours. The solid obtained on pouring the reaction mixture into excess of ice water was filtered off, recrystallised from ethyl alcohol, and finally distilled under reduced pressure to remove last traces of ethyl alcohol. The main fraction distilled at 128—130°/80 mm., and froze at 19°.

Polarisation Measurements.—These were made by using the apparatus described in Part I (*loc. cit.*). In the following tables the symbols have the usual significance.

f_2.	$d_4^{25°}$.	$\epsilon_{25°}$.	P_2.	f_2.	$d_4^{25°}$.	ϵ_{25}.	P_2.
*Ethyl alcohol in isopropyl ether.*				*Ethyl alcohol in dioxan.*			

Ethyl alcohol in isopropyl ether. / *Ethyl alcohol in dioxan.*

f_2.	$d_4^{25°}$.	$\epsilon_{25°}$.	P_2.	f_2.	$d_4^{25°}$.	ϵ_{25}.	P_2.
0·0000	0·71849	3·9511	—	0·0000	1·0272	2·2874	—
0·021581	0·71953	4·0738	92·6	0·024672	1·0229	2·4021	80·6
0·027171	0·71984	4·1066	92·6	0·037793	1·0209	2·4682	81·0
0·045242	0·72081	4·2190	93·2	0·047006	1·0194	2·5220	82·7
0·050011	0·72104	4·2490	93·2	0·07072	1·0151	2·6545	83·0
0·055746	0·72148	4·2878	93·2	0·08905	1·0120	2·7660	83·3
0·068176	0·72186	4·3705	93·4	0·11593	1·0073	2·9445	83·8
0·08093	0·72252	4·4573	93·4	0·13137	1·0045	3·0437	83·3
0·087129	0·72278	4·5010	93·0	0·15299	1·0008	3·2077	83·5
0·10565	0·72393	4·6357	92·5	0·24135	0·98395	3·9985	83·1
0·11609	0·72461	4·7219	92·68	0·29178	0·97411	4·5555	82·1

$_\infty P_2 = 91·9.$ / $_\infty P_2 = 79·2.$

Ethyl alcohol in amyl ether.

				0·0000	0·77165	2·8220	—
*Ethyl alcohol in n-butyl ether.*				0·019581	0·77175	2·8989	104·9

Ethyl alcohol in n-butyl ether.

f_2	$d_4^{25°}$	$\epsilon_{25°}$	P_2	f_2	$d_4^{25°}$	ϵ_{25}	P_2
0·0000	0·76569	3·0806	—	0·039928	0·77187	2·9475	100·7
0·039544	0·76611	3·2382	98·0	0·056048	0·77194	2·9982	99·1
0·060722	0·76633	3·3275	97·2	0·07675	0·77198	3·0689	98·4
0·094229	0·76680	3·4787	96·2	0·12261	0·77225	3·2353	97·0
0·12707	0·76703	3·6434	95·9	0·22817	0·77277	3·7132	95·1
0·14974	0·76728	3·7612	95·1	0·32833	0·77337	4·3804	94·8
0·20414	0·76793	4·0993	94·8				

$_\infty P_2 = 99·5.$ / $_\infty P_2 = 112.$

Cryoscopic Measurements.—These were made with the Beckmann apparatus, the usual precautions being adopted. In diphenyl ether excessive supercooling (3—4°) takes place and a modification of the usual procedure, suggested by Dr. R. Wright of this University, has been successfully used. A fair amount of the solvent is frozen out from the solution and allowed to become warm. Until the freezing point is reached the rate of heating is very slow and the change of rate once the freezing point is passed is very marked. In practice, it is sufficient to stir at a steady rate and count the number of strokes for each successive rise in temperature of 0·01°. Δt is the observed depression of freezing point when w g. of solute are dissolved in W g. of solvent.

Solvent.	Solute.	W.	w.	Δt.	K.
Dioxan	Naphthalene	25·46	0·3274	0·34°	4·87
			0·4313	0·63	4·75
	Dinitrobenzene	21·27	0·4297	0·57	4·74
			0·6841	0·91	4·75
Ethyl cetyl ether	Benzene	11·07	0·1492	0·78	4·51
			0·2250	1·15	4·42
	Hexane	13·64	0·1013	0·39	4·52
			0·1800	0·69	4·50
Diphenyl ether	Naphthalene	21·09	0·2574	0·72	7·55
			0·4385	1·24	7·63

Average values of K are : dioxan 4·78, ethyl cetyl ether 4·49, diphenyl ether 7·59. For dioxan, Oxford (*Biochem J.*, 1935, **28**, 1326) gives 4·7, Eigenberger (*J. pr. Chem.*, 1931, **130**, 75) 4·8, and Kraus and Vingee (*J. Amer. Chem. Soc.*, 1934, **56**, 511) 4·63. For diphenyl ether, Durand and Rouge (*Bull. Soc. chim.*, 1925, **37**, 697) give 7·96.

In the following table the solute in each case is ethyl alcohol.

$w.$	$\Delta t.$	$M.$	$w.$	$\Delta t.$	$M.$	$w.$	$\Delta t.$	$M.$
In dioxan (W = 21·28).			In ethyl cetyl ether (W = 13·60).			In diphenyl ether (W = 19·90).		
0·1571	0·71°	49·7	0·0643	0·37°	57·4	0·3710	1·87°	75·7
0·3082	1·35	51·3	0·1216	0·64	62·7	0·5818	2·42	91·7
0·5474	2·41	53·5	0·1655	0·84	65·0	0·8808	2·94	114·6
0·7883	3·22	55·0	0·2265	1·05	71·2	In diphenyl ether (W = 19·50).		
1·0564	4·14	57·3	0·2801	1·24	74·6	0·3005	1·71	68·0
						0·4743	2·28	81·0
						0·6081	2·61	90·7

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