867. *Dielectric Polarisation Studies of the Formation of Hydrogen-bond Complexes by Alcohols.*

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The apparent molecular polarisations of *n*- and *tert.*-butyl alcohols at zero concentration in various benzene–triethylamine mixtures, and of triethylamine at zero concentration in various mixtures of benzene with the alcohols, have been determined. From the latter results the equilibrium constants for the association of triethylamine with the monomeric alcohol molecules and the effective molecular polarisations and dipole moments of the complexes have been deduced. Association of *n*-butyl alcohol with triethylamine occurs more readily than with pyridine, but that of *tert.*-butyl alcohol occurs less readily. No complex formation between *n*-butyl alcohol and *n*-butyl sulphide, dimethylaniline, or benzotrifluoride, between *tert.*-butyl alcohol and dimethylaniline, or between benzyl alcohol and benzoquinone could be detected by polarisation measurements on dilute solutions. From measurements on benzene solutions at 25° the following dipole moments have been derived: triethylamine 0·80, *n*-butyl sulphide 1·61, and benzotrifluoride 2·56 D.

WHEN this work was begun in 1948, it was known that the apparent molecular polarisations of alcohols in benzene are increased by the presence of small concentrations of pyridine, and that the apparent molecular polarisations of phenols and aromatic amines are higher in dioxan or ether than in benzene. These phenomena were attributable to hydrogen-bond formation between the hydroxylic or amino-hydrogen atoms and the nitrogen atoms of pyridine molecules or oxygen atoms of dioxan or ether molecules. As, therefore, polarisation measurements appeared to present a method of detecting even a weak tendency for intermolecular hydrogen-bonding interaction, it was decided to study the apparent dielectric polarisations of alcohols in benzene solutions in the presence of other compounds the molecules of which contain atoms which may act as electron donors for hydrogen-bond formation, but which contain no hydrogen atoms likely to participate in hydrogen-bonding association. Such compounds include tertiary aliphatic and mixed aliphatic–aromatic amines, ethers, and thio-ethers, and certain ketones and fluorine-containing compounds. Measurements have therefore been made on benzene solutions containing an alcohol together with triethylamine, dimethylaniline, *n*-butyl sulphide, benzoquinone, or benzotrifluoride, and the results compared with those to be expected if the polarisations of the components remained the same as when they are present alone in benzene solution at similar concentrations. Only in the systems containing triethylamine has any detectable enhancement of the polarisation been observed, however, and hence these systems have been studied in greater detail.

For this purpose the dielectric constants, refractive indices, and specific volumes of solutions of triethylamine in benzene and in various mixtures of benzene with *n*- or *tert.*-butyl alcohol have been measured. The results are shown in Table 1, where w_A' and w_B indicate the weight fractions of the alcohol in the solvent mixture and of triethylamine in the solutions, respectively, and the other symbols have their usual significance. In both systems the apparent molecular polarisation of the triethylamine shows a significant dependence on the concentrations both of the amine itself and of the alcohol, but the corresponding value of the molecular refraction is not increased by the presence of alcohol. From these measurements, together with the results obtained for solutions of the alcohols

TABLE 1. *Polarisation data for triethylamine at 25°.*

Solutions in benzene

100w_2	ε	v	n_D	p (c.c.)	P_2 (c.c.)	$[R_D]_2$ (c.c.)
0·0000	2·2725	1·14458	1·4980	0·34088	—	—
0·8324	2·2747	1·14663	1·4969	0·34191	47·0	33·6
1·5693	2·2767	1·14842	1·4959$_5$	0·34282	47·0	33·6
2·5213	2·2793	1·15069	1·4948	0·34399	47·0	33·8
3·9361	2·2833	1·15416	1·4930	0·34579	47·1	33·6
5·8653	2·2887	1·15883	1·4906	0·34821	47·1	33·7
0·0000	2·2725	1·14456	1·4979	0·34088	—	—
0·8988	2·2748	1·14675	—	0·34201	47·0	—
1·3291	2·2760	1·14793	—	0·34255	47·2	—
2·2543	2·2783	1·15020	—	0·34368	47·1	—
3·3420	2·2814	1·15282	—	0·34502	47·0	—
3·6921	2·2822	1·15363	—	0·34543	47·0	—
5·5640	2·2871	1·15765	—	0·34756	46·8	—
0·0000	—	1·14456	1·4979	—	—	—
0·7617	—	1·14641	1·4969	—	—	33·4
1·5175	—	1·14833	1·4959$_5$	—	—	33·8
2·4187	—	1·15059	1·4947$_5$	—	—	33·7
3·0877	—	1·15215	1·4940	—	—	33·8
3·8543	—	1·15395	1·4930	—	—	33·7

*Solutions in benzene–*n*-butyl alcohol mixtures*

100w_A'	100w_B	ε	v	n_D	p (c.c.)	P_B (c.c.)	$[R_D]_B$ (c.c.)
1·119	0·0000	2·3172	1·14603	1·4965	0·34967	—	—
	0·5177	2·3221	1·14717	1·4959	0·35091	59·6	33·7
	1·5613	2·3304	1·14957	1·4947	0·35317	58·1	33·9
	2·4764	2·3360	1·15165	1·4935$_5$	0·35485	56·6	33·7
	3·2378	2·3396	1·15362	1·4925$_5$	0·35611	55·5	33·7
	4·2270	2·3437	1·15570	1·4914	0·35750	54·1	33·7
	6·9467	2·3513	1·16213	1·4882	0·36090	51·7	33·7
3·882	0·0000	2·4348	1·14926	1·4931	0·37182	—	—
	0·7725	2·4536	1·15079	1·4923	0·37561	87·3	33·8
	1·3628	2·4658	1·15194	1·4916	0·37810	84·2	33·3
	2·6619	2·4866	1·15463	1·4902	0·38258	78·5	33·4
	3·4780	2·4964	1·15640	1·4894	0·38485	75·5	33·6
	4·7494	2·5087	1·15912	1·4880	0·38786	71·8	33·6
	5·4927	2·5138	1·16070	1·4872	0·38926	69·7	33·6
6·559	0·0000	2·5498	1·15213	1·4899	0·39245	—	—
	0·5638	2·5745	1·15316	1·4892	0·39691	119·8	—
	1·2026	2·5950	1·15437	1·4886$_5$	0·40070	109·1	33·2
	1·8453	2·6157	1·15556	1·4880$_5$	0·40449	105·7	33·4
	2·7335	2·6366	1·15725	1·4872$_5$	0·40847	99·0	33·6
	4·7409	2·6702	1·16127	1·4852$_5$	0·41530	88·5	33·5
	5·9471	2·6848	1·16420	1·4839	0·41868	84·3	33·8
10·486	0·0000	2·7484	1·15634	1·4849	0·42578	—	—
	0·8836	2·7958	1·15779	1·4842$_5$	0·43353	131·8	34·0
	1·7344	2·8344	1·15923	1·4836	0·43987	125·3	33·6
	2·5175	2·8639	1·16060	1·4829	0·44475	119·3	33·5
	3·3977	2·8918	1·16219	1·4820	0·44945	113·6	33·5
	4·5695	2·9212	1·16435	1·4809	0·45455	106·9	33·4
	7·0021	2·9581	1·16897	1·4786	0·46166	94·9	33·4
			*Solutions in benzene–*tert.*-butyl alcohol mixtures*				
1·025	0·0000	2·3101	1·14662	1·4964	0·34853	—	—
	0·9762	2·3141	1·14892	1·4952	0·34997	50·2	33·8
	1·8479	2·3175	1·15098	1·4941	0·35123	50·0	33·7
	2·8360	2·3212	1·15331	1·4929	0·35262	49·9	33·7
	3·9042	2·3249	1·15583	1·4915	0·35408	49·7	33·9
	4·8634	2·3281	1·15810	1·4903	0·35537	49·5	33·5
	5·9631	2·3316	1·16069	1·4891	0·35681	49·3	33·7

TABLE 1. (*Continued.*)

$100w_A'$	$100w_B$	ε	v	n_D	p (c.c.)	P_B (c.c.)	$[R_D]_B$ (c.c.)
			Solutions in benzene–tert.*-butyl alcohol mixtures*				
2·345	0·0000	2·3586	1·14902	1·4941$_5$	0·35816	—	—
	0·8858	2·3635	1·15110	1·4931	0·35970	53·8	33·9
	2·1451	2·3702	1·15395	1·4916	0·36180	53·4	33·7
	2·4187	2·3716	1·15460	1·4913	0·36226	53·4	33·8
	3·5276	2·3764	1·15701	1·4900	0·36389	52·7	33·6
	4·4192	2·3807	1·15915	1·4889$_5$	0·36534	52·7	33·7
	5·6938	2·3856	1·16206	1·4874	0·36714	52·2	33·6
3·723	0·0000	2·4080	1·15149	1·4921	0·36781	—	—
	1·0824	2·4149	1·15399	1·4909	0·36983	56·1	34·1
	1·8890	2·4193	1·15577	1·4900	0·37119	55·4	33·9
	2·6795	2·4237	1·15749	1·4891	0·37252	55·0	33·8
	3·7054	2·4288	1·15976	1·4879	0·37416	54·6	33·7
	4·7975	2·4342	1·16221	1·4867	0·37591	54·3	33·7
	6·0594	2·4398	1·16499	1·4852$_5$	0·37779	53·9	33·7
6·239	0·0000	2·4892	1·15593	1·4887	0·38346	—	—
	0·8406	2·4958	1·15772	1·4878	0·38519	59·6	33·7
	1·7197	2·5025	1·15960	1·4869	0·38696	59·4	33·7
	2·7528	2·5093	1·16179	1·4858	0·38886	58·7	33·7
	3·6618	2·5149	1·16376	1·4849	0·39048	58·2	33·7
	4·9925	2·5224	1·16661	1·4835$_5$	0·39289	57·9	33·7
	6·1538	2·5293	1·16912	1·4822	0·39474	57·3	33·6
7·770	0·0000	2·5415	1·15862	1·4865	0·39327	—	—
	0·8557	2·5494	1·16040	1·4856	0·39520	62·6	33·4
	1·7972	2·5566	1·16236	1·4846	0·39707	61·2	33·5
	2·7325	2·5638	1·16426	1·4836	0·39893	60·8	33·5
	3·5759	2·5694	1·16603	1·4828	0·40048	60·2	33·5
	4·4710	2·5753	1·16787	1·4818	0·40211	59·8	33·4
	6·1120	2·5851	1·17130	1·4801	0·40493	59·1	33·4

in benzene,[1] the apparent molecular polarisations of triethylamine at zero concentration in the alcohol–benzene mixtures, $(P_{B_\infty})_{AS}$, and of the alcohols at zero concentration in various triethylamine–benzene mixtures, $(P_{A_\infty})_{BS}$, have been calculated. These are summarised in Table 2, where α, β, and γ are the limiting values of $d\varepsilon/dw$, dv/dw, and dn^2/dw, respectively, at zero concentration of solute, and $(P_{A_\infty})_S$ and $(P_{B_\infty})_S$ are the molecular polarisations of the solutes at zero concentration in benzene alone.

It has been shown [2] that if two solutes A and B associate to form an unstable compound AB, the molecular polarisation of which, at zero concentration in an inert solvent, is $(P_{AB_\infty})_S$, it should be possible to deduce the values of $(P_{AB_\infty})_S$ and of K, the association constant of the complex, from dielectric-polarisation measurements alone. If the active masses of A, B, and AB can be represented by their concentrations in mole/c.c., and M_B is the molecular weight of B, a plot of $1/\{(P_{A_\infty})_{BS} - (P_{A_\infty})_S\}$ against $M_B v_{BS}/w_B'$ should be linear, with a slope $1/K\Delta P$ and an intercept on the axis for the former of $1/\Delta P$, where $\Delta P = (P_{AB_\infty})_S - (P_{A_\infty})_S - (P_{B_\infty})_S$. The application of this method gives reasonable values for the dipole moments and association constants of the complexes formed by pyridine with *n*- and *tert.*-butyl alcohol and diphenylmethanol.[3] The values for the present systems of the functions which require plotting are shown in the last two columns of Table 2. They also lead to very good straight lines, and the values of the slopes and intercepts obtained by application of the least-squares method, and the quantities derived from them, are shown in Table 3.

These results should apply to the association of triethylamine molecules with monomeric alcohol molecules. On the other hand the values of $(P_{B_\infty})_{AS}$ apply to systems in which the alcohols themselves are strongly associated, a circumstance which must affect the association of the triethylamine with the alcohol. Hence, as was found for the systems

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[1] Boud, Cleverdon, Collins, and Smith, *J.*, 1955, 3793.

[2] Few and Smith, *J.*, 1949, 2781.

[3] Cleverdon, Collins, and Smith, preceding paper.

involving pyridine and *n*- or *tert.*-butyl alcohol, the $(P_{B_\infty})_{AS} - (P_{B_\infty})_S$ values are greater than would be expected from the treatment of the systems as solutions of alcohols in triethylamine–benzene mixtures, and hence the plots of $1/\{(P_{B_\infty})_{AB} - (P_{B_\infty})_S\}$ against $M_A v_{AS}/w_A'$ do not superpose upon those for the reverse system, although the results for the *tert.*-butyl alcohol–triethylamine system are much more nearly superposable than those for the *tert.*-butyl alcohol–pyridine system. In each case, however, the divergences are in the same sense as was observed for the systems formerly studied, and hence support the explanation then offered.

TABLE 2. *Summary of polarisation data for butyl alcohol–triethylamine–benzene systems.*

$100w_A'$	α	β	$-\gamma$	$(P_{B_\infty})_{AS}$ (c.c.)	$[R_D]_B$ (c.c.)	$M_A v_{AS}/w_A'$	$\dfrac{10^4}{(P_{B_\infty})_{AS} - (P_{B_\infty})_S}$
		Triethylamine in n-*butyl alcohol–benzene mixtures*					
0·000	0·264	0·244	0·372	47·0	33·8	—	—
1·119	1·005	0·226	0·359	60·5	33·8	7591	741
3·882	2·65	0·196	0·327	91·6	33·8	2194	224
6·559	4·39	0·181	0·301	120·1	33·7	1302	137
10·486	5·82	0·162	0·270	139·7	33·6	817	108
		Triethylamine in tert.-*butyl alcohol–benzene mixtures*					
1·025	0·42	0·236	0·360	50·4	33·8	8292	2941
2·345	0·59	0·229	0·352	54·3	33·8	3632	1370
3·723	0·66	0·223	0·336	56·3	33·8	2292	1075
6·239	0·84	0·213	0·321	60·5	33·7	1373	741
7·770	0·91	0·207	0·312	62·4	33·5	1105	649

$100w_B'$	v_{BS}	$(P_{A_\infty})_{BS}$ (c.c.)	$M_B v_{BS}/w_B'$	$\dfrac{10^4}{(P_{A_\infty})_{BS} - (P_\infty)_S}$
	n-*Butyl alcohol in triethylamine–benzene mixtures*			
0·000	1·14458	80·7	—	—
1·000	1·14702	89·7	11,606	1111
2·000	1·14946	95·2	5815	680
3·000	1·15190	99·3	3885	538
4·000	1·15434	102·0	2920	460
5·000	1·15677	104·5	2341	420
6·000	1·15921	106·5	1955	388
	tert.-*Butyl alcohol in triethylamine–benzene mixtures*			
0·000	1·14458	80·7	—	—
1·000	1·14702	83·0	11,606	4348
2·000	1·14946	85·0	5815	2326
3·000	1·15190	86·8	3885	1639
4·000	1·15434	88·4	2920	1298
5·000	1·15677	89·9	2341	1087
6·000	1·15921	91·3	1955	943

TABLE 3. *Association constants in benzene solution and dipole moments of complexes of triethylamine with alcohols.*

	$1/K\Delta P$ $\times 10^8$	$1/\Delta P$ $\times 10^4$	K $\times 10^{-1}$	ΔP (c.c.)	$(P_{AB_\infty})_S$ (c.c.)	$[R_D]_{AB}$ (c.c.)	μ_{AB} (D)
n-Butyl alcohol	749	247	330	40	168	56	2·34
tert.-Butyl alcohol	3491	300	86	33	161	57	2·25

As is to be expected from the relative strengths of the two bases concerned, the value of K for the system *n*-butyl alcohol–triethylamine is appreciably greater than that for the system *n*-butyl alcohol–pyridine (20×10^2), and is very close to that found for the system *n*-heptyl alcohol–trimethylamine by Denyer, Gilchrist, Pegg, Smith, Tomlinson, and Sutton,[4] using a vapour-partition method (35×10^2). With *tert.*-butyl alcohol, on the other hand, association with triethylamine occurs less readily than with pyridine : this may be ascribed to steric effects which are unfavourable to association, since in certain

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[4] Denyer, Gilchrist, Pegg, Smith, Tomlinson, and Sutton, *J.*, 1955, 3889.

conformations the methyl groups of the alcohol and of the triethylamine molecule approach one another fairly closely.

If the apparent dipole moments of the complexes are interpreted as the vector sums of the moments of the alcohols (1·69 D) and of triethylamine (0·80 D), they indicate that the dipoles in the alcohols are directed at angles of 43° and 54½° to the axis of the H–O bond in *n*- and *tert.*-butyl alcohol, respectively. These angles differ in the same sense, and by about the same amount, as was inferred from the results for the complexes with pyridine (60° and 72°, respectively). The two sets of results can be reconciled if it is supposed that there is a small contribution to the moment through a redistribution of the electron density in the O–H···N system, as has been suggested by Hulett, Pegg, and Sutton[5] for such association, and also a consequential modification in the remaining bond moments in the molecules. The difference between the results for the triethylamine and pyridine complexes corresponds to an additional moment along the H–O bond axis of 0·18 and 0·25 D in the *n*- and *tert.*-butyl alcohol complexes, respectively.

The results of measurements on the other systems studied are given in Table 4. For the solutions in the mixed solvents the apparent values of the molecular polarisation of the solute (P_2) are compared with the values found for the same concentrations in benzene (P'). Except for the highest concentrations of benzyl alcohol in the benzene–*p*-benzoquinone mixture, the values of P_2 are within experimental error of, or less than, P_2'. It must be inferred, therefore, that there is insufficient complex formation in these systems at the concentrations studied to produce a significant change in the dielectric polarisation. The fact that for solutions of both *n*- and *tert.*-butyl alcohol in benzene–dimethylaniline mixtures the values of P_2 are lower than in benzene itself, and by an almost constant amount in each case, probably arises from a reduction of the effective molecular polarisation of the dimethylaniline through the increase in the dielectric constant of the medium arising from the addition of the butyl alcohol. This view seems to be supported by the fact that the molecular polarisation values for benzotrifluoride in benzene–*n*-butyl alcohol mixtures are almost exactly those to be expected in benzene solutions of the same dielectric constant. Such results give a warning of the care which should be taken in interpreting small changes in dielectric polarisation quantitatively in terms of hydrogen-bonding association when the effective dipole moment of one of the molecular species concerned is strongly dependent on the dielectric constant of the medium. The alcohols and triethylamine studied here do not suffer from this defect, nor does pyridine, which was used in the previous investigation.

The molecular polarisations at zero concentration, molecular refractions, and dipole moments deduced from the measurements on the various components separately in benzene solution are shown in Table 5, together with the corresponding figures for *p*-benzoquinone in carbon tetrachloride solution.

Our values of $P_{2\infty}$ and μ for triethylamine are in good agreement with those of Higasi,[6] but are appreciably lower than those reported by Barclay, Le Fèvre, and Smythe (50·1 c.c. and 0·91 D).[7] This arises from the fact that the latter authors found a considerable departure from linearity in the ε–w_2 plot, leading to a fairly rapid increase in $\Delta\varepsilon/w_2$ with decrease in w_2. We find ε to be sensibly linear with w_2 over the concentration range studied, the slope α being almost identical with the value of $\Delta\varepsilon/w_2$ found by Barclay, Le Fèvre, and Smythe at the highest concentrations they studied. We also find $[R_D]_2$ to be higher than the value (33·1 c.c.) reported by them, and to agree with the value found by Vogel,[8] which is also indicated by our own measurements on the pure liquid.

The dipole moment found for benzotrichloride is close to previous values (2·56,[9] 2·60 D[10]). The mesomeric mechanism suggested by Roberts, Webb, and McElhill[10] to account for the fact that this moment is higher than that of trifluoromethyl*cyclo*hexane

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[5] Hulett, Pegg, and Sutton, *J.*, 1955, 3901.
[6] Higasi, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, 1937, **31**, 211.
[7] Barclay, Le Fèvre, and Smythe, *Trans. Faraday Soc.*, 1950, **46**, 812.
[8] Vogel, *J.*, 1948, 1830.
[9] Freiser, Hobbs, and Gross, *J. Amer. Chem. Soc.*, 1949, **71**, 111,
[10] Roberts, Webb, and Elhill, *ibid.*, 1950, **72**, 408,

TABLE 4. *Polarisation data.*

n-*Butyl sulphide in benzene*

$100w_2$	ε	v	n_D	P_2 (c.c.)	R_D (c.c.)
0·0000	2·2725	1·14458	1·4979	—	—
1·1666	2·2924	1·14532	1·4972	99·8	—
1·9566	2·3062	1·14593	1·4967	100·0	46·9
2·5968	2·3173	1·14629	1·4963	99·8	46·8
3·8298	2·3382	1·14713	1·4957	99·6	47·0
5·0269	2·3593	1·14783	1·4949	99·4	46·9
5·4504	2·3668	1·14816	1·4947	99·4	46·9

Benzotrifluoride in benzene

$100w_2$	ε	v	n_D	P_2 (c.c.)	R_D (c.c.)
0·0000	2·2725	1·14458	1·4979	—	—
0·9262	2·3156	1·14198	1·4972$_5$	164·0	31·2
1·3762	2·3359	1·14074	1·4969	162·5	31·0
1·5063	2·3423	1·14039	1·4968	162·5	31·0
2·3891	2·3833	1·13796	1·4961	161·2	30·8
2·6512	2·3950	1·13720	1·4959	160·4	30·8
3·2767	2·4248	1·13545	1·4954	160·0	30·7
4·0261	2·4596	1·13340	1·4948$_5$	159·2	30·9
4·1568	2·4669	1·13299	1·4947$_5$	159·4	30·8
5·4780	2·5295	1·12935	1·4938	157·7	30·9
7·0079	2·6060	1·12482	1·4926	156·8	30·7

p-*Benzoquinone in benzene*

$100w_2$	ε	v	n_D	P_2 (c.c.)	R_D (c.c.)
0·0000	2·2725	1·14457	1·4979	—	—
0·5141	2·2752	1·14300	1·4980	37·7	28·5
0·7832	2·2762	1·14220	1·4981	36·7	28·4
0·9020	2·2770	1·14182	1·4981	37·2	28·0
1·0770	2·2778	1·14129	1·4982	37·2	28·7
1·3365	2·2792	1·14042	1·4982	37·0	28·0
1·8685	2·2818	1·13881	1·4984	37·0	28·0
1·9149	2·2820	1·13871	1·4985	37·1	28·7
2·0509	2·2830	1·13827	1·4985	37·3	28·5
2·3884	2·2847	1·13728	1·4985	37·3	28·2
3·2314	2·2889	1·13467	1·4989	37·2	28·4
3·5536	2·2908	1·13362	1·4989	37·3	28·2
5·2114	2·2990	1·12860	1·4995	37·1	28·4

p-*Benzoquinone in carbon tetrachloride*

$100w_2$	ε	v	n_D	P_2 (c.c.)	R_D (c.c.)
0·0000	2·2252	0·63135	1·4574	—	—
0·4894	2·2301	0·63244	1·4580	38·1	29·4
0·7298	2·2322	0·63295	1·4583	37·5	29·3
1·3577	2·2387	0·63431	1·4590	38·0	29·2

n-*Butyl alcohol in benzene* + n-*butyl sulphide* (5·72 *wt.* %)

$100w_2$	ε	v	n_D	P_2 (c.c.)	R_D (c.c.)	P_2' (c.c.)
0·0000	2·3716	1·14830	1·4943	—	—	—
0·9129	2·4078	1·14936	1·4934	82·0	—	82·1
1·9075	2·4501	1·15059	1·4920	83·6	22·3	83·4
2·6053	2·4807	1·15134	1·4913	84·1	22·4	83·9
4·0779	2·5448	1·15304	1·4895	84·2	22·3	84·3
4·7938	2·5763	1·15371	1·4889	84·1	22·2	84·2
5·3422	2·6007	1·15427	1·4880	84·0	22·2	84·2

n-*Butyl alcohol in benzene + dimethylaniline* (6·01 *wt.* %)

$100w_2$	ε	v	n_D	P_2 (c.c.)	R_D (c.c.)	P_2' (c.c.)
0·0000	2·4273	1·13894	1·5011	—	—	—
0·9009	2·4606	1·14020	1·5000	78·0	—	82·1
1·7061	2·4937	1·14116	1·4989	80·0	22·3	83·2
2·4613	2·5264	1·14209	1·4977	81·3	21·8	83·8
3·2811	2·5612	1·14318	1·4964	81·7	21·8	84·1
4·4026	2·6115	1·14438	1·4953	82·3	22·0	84·3
5·1695	2·6458	1·14530	1·4941$_5$	82·5	21·8	84·2

tert.-*Butyl alcohol in benzene + dimethylaniline* (7·60 *wt.* %)

$100w_2$	ε	v	n_D	P_2 (c.c.)	R_D (c.c.)	P_2' (c.c.)
0·0000	2·4634	1·13733	1·5022	—	—	—
0·9163	2·4965	1·13922	1·5008	78·2	22·9	80·5
1·7709	2·5247	1·14093	1·4993	76·1	22·3	80·3
2·7839	2·5599	1·14289	1·4979	75·8	22·7	79·6
3·8084	2·5950	1·14480	1·4964	75·3	22·7	78·5
4·4623	2·6172	1·14594	1·4959	74·9	22·6	77·7
5·0029	2·6330	1·14692	1·4957	74·1	22·6	77·2

Benzyl alcohol in benzene + p-*benzoquinone* (5·43 *wt.* %)

$100w_2$	ε	v	n_D	P_2 (c.c.)	R_D (c.c.)	P_2' (c.c.)
0·0000	2·3008	1·12798	1·4994	—	—	—
1·1329	2·3352	1·12601	1·4998$_5$	91·0	32·8	91·4
2·2608	2·3731	1·12411	1·5003	93·3	32·8	93·5
3·5633	2·4199	1·12182	1·5008	95·3	32·7	95·2
5·3419	2·4873	1·11869	1·5017	96·9	32·9	96·3
7·9736	2·5926	1·11407	1·5024$_5$	98·2	32·6	97·0

Benzotrifluoride in benzene + n-*butyl alcohol* (6·194 *wt.* %)

$100w_2$	ε	v	n_D	P_2 (c.c.)	R_D (c.c.)	P_2' (c.c.)
0·0000	2·5511	1·15220	1·4900	—	—	—
0·8089	2·5885	1·14983	1·4894$_5$	154·5	—	164·0
1·2792	2·6107	1·14849	1·4891	154·8	—	162·8
2·0323	2·6453	1·14635	1·4886	153·3	—	161·4
2·8902	2·6858	1·14393	1·4879$_5$	152·9	—	160·3
4·3920	2·7568	1·13957	1·4870	151·1	—	159·2
5·5897	2·8120	1·13613	1·4861	149·3	—	157·6

TABLE 5.

Compound		$10^3\alpha$	$10^3\beta$	$10^3\gamma$	$P_{2\infty}$ (c.c.)	$[R_D]_2$ (c.c.)	μ (D)
Triethylamine	(B)	264	244	−372	47·0	33·8	0·80
n-Butyl sulphide	(B)	1725	66	−178	100·1	46·9	1·61
Benzotrifluoride	(B)	4610	−279	−226	164·4	30·8	2·56
p-Benzoquinone	(B)	508	−306	88	37·3	28·4	—
p-Benzoquinone	(C)	994	219	353	38·0	29·3	—

(B) = Benzene solution; (C) = carbon tetrachloride solution.

would seem to favour the possibility of hydrogen-bonding by the fluorine atoms, but any such association which occurs in the system studied is apparently too weak to be detected by this dilute-solution method.

Our value for the moment of *n*-butyl sulphide is slightly higher than values previously reported (1·57,[11] 1·56 D [12]). This is appreciably greater than the moment of an aliphatic ether (~1·22 D), a fact which supports the view that the association which leads to an increase in polarisation in solutions of alcohols in ethers is not a simple dipole association, since the latter type of association should occur even more strongly with thio-ethers.

Both our $P_{2\infty}$ and $[R_D]$ values for benzoquinone in benzene are appreciably lower than those reported by Le Fèvre and Le Fèvre,[13] but close to those of Hammick, Hampson, and Sutton,[14] as is our $P_{2\infty}$ value for carbon tetrachloride solutions. We find the $[R_D]$ value in the latter solvent to be slightly higher than in benzene, however. As a result, the differences between $P_{2\infty}$ and $[R_D]$, attributable to atom polarisation, are 8·9 and 8·7 c.c. in benzene and carbon tetrachloride, respectively, as compared with Hammick, Hampson, and Sutton's values of 8·83 and 9·59 c.c., respectively, and Coop and Sutton's value of 8·2 c.c. for the vapour.[15]

EXPERIMENTAL

Materials.—Benzene, *n*- and *tert.*-butyl alcohol, benzyl alcohol, and dimethylaniline were purified as described previously.[1,16] Commercial pure triethylamine was kept for some weeks over potassium hydroxide and distilled twice from this reagent, the middle fractions being collected. The product used had n_D^{25} 1·3980, d_4^{25} 0·72350, whence $[R_D]$ = 33·8 c.c. *n*-Butyl sulphide, prepared from pure *n*-butyl bromide and sodium sulphide by Bost and Conn's method,[17] had n_D^{25} 1·4505, d_4^{25} 0·8366, $[R_D]$ 47·0 c.c. Pure commercial benzotrifluoride was dried ($CaCl_2$) and fractionally distilled, the sample used having b. p. 102·8°/778 mm., n_D^{25} 1·41215, d_4^{25} 1·18132, $[R_D]$ 30·8 c.c. *p*-Benzoquinone was prepared by oxidising quinol with sodium dichromate and sulphuric acid.[18] It was recrystallised twice from benzene and finally sublimed: it had m. p. 113·6°.

Methods.—The dielectric constants of the solutions, relative to that of pure benzene, were measured with a modified form of the heterodyne-beat apparatus described by Few, Smith, and Witten.[19] The densities were measured with a pyknometer (about 10 c.c. capacity), and the refractive indices with both Pulfrich and Abbé refractometers. All measurements were made at 25°.

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[*Received, June 6th,* 1956.]

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