The Molecular Polarisation and Association of Some Hydroxylic Compounds in Benzene Solution.

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The dielectric constants, specific volumes, and refractive indices of benzene solutions of *n*- and *tert.*-butyl and benzyl alcohols, diphenylmethanol, and phenol have been measured over the concentration range 0·2—7% (w/w), and the apparent molecular polarisations of the solutes at each concentration evaluated. Cryoscopic measurements have also been made on benzene solutions of *n*- and *tert.*-butyl alcohols and of diphenylmethanol. For each compound the course of the molecular polarisation–concentration curve is anomalous compared with that for a non-associating solute, but it has been interpreted in terms of the geometrical form of the molecules concerned and their association. Owing to this anomalous behaviour the results cannot be extrapolated to zero concentration so accurately as for normal solutes. From the measurements at the lowest concentrations, however, and the total distortion polarisation being assumed to be equal to the molecular refraction for the Na-D line, the values obtained for the apparent dipole moments of the monomeric forms in benzene solution are : *n*-butyl alcohol 1·69, *tert.*-butyl alcohol 1·69, diphenylmethanol 1·62, benzyl alcohol 1·67, and phenol 1·45 D.

OWING to the strong tendency of alcohols to associate, their solutions in non-polar solvents show a variation of dielectric polarisation with concentration which is anomalous compared with that for solutions of a normal non-associating solute. The most firmly established feature is that the values of the molecular polarisation (P_2) of certain alcohols, based on the molecular weight of the monomeric alcohol and calculated on the assumption that the molecular polarisation of the solvent remains constant, pass through a maximum, often within the concentration range 40—60 mol.-% alcohol.

The evidence regarding the behaviour at low concentrations is more conflicting. Smyth and Stoops (*J. Amer. Chem. Soc.*, 1929, **51**, 3312), Hennings (*Z. phys. Chem.*, 1935, **28**, *B*, 267), Müller and Mortier (*Physikal. Z.*, 1935, **36**, 371), and Hoecker (*J. Chem. Phys.*, 1936, **4**, 431) all found that the P_2 values of ethyl or *n*-butyl alcohol decrease with increasing concentration and pass through a minimum below 1 mol.-%, before increasing to the maximum value. On the other hand, Maryott (*J. Amer. Chem. Soc.*, 1941, **63**, 3079) was unable to find any such minima. Smyth and Stoops also reported that the P_2 values for various alcohols at concentrations below about 1 mol.-% in hexane or heptane solution appeared to increase with rise of temperature, instead of decreasing as would be expected on the Debye theory. Since the dipole moment of a monomeric alcohol molecule should be almost independent of the orientation of the hydroxyl group with respect to the carbon chain, such behaviour is possible only if P_2 for the unassociated molecules is greater than its apparent value for the associated molecules.* Even then it should occur only at concentrations at which the degree of association is fairly high, so that there is an appreciable

* Here, as elsewhere in this paper, P_2 for a compound in the associated state is taken as the value based on the molecular weight of the monomer.

increase in the proportion of non-associated molecules when the temperature is raised. Smyth and Stoops's extrapolation of their results, however, suggests that the increase in P_2 with rise of temperature becomes a maximum at zero concentration, which seems to be impossible, as the $P_{2\infty}$ value should apply to the unassociated molecules.

Before making a quantitative study of the marked changes in the apparent molecular polarisation of alcohols produced by the addition of small concentrations of nitrogenous bases (Cleverdon and Smith, *Chem. and Ind.*, 1948, 23), it was necessary to reinvestigate the molecular polarisations of certain alcohols at low concentrations in benzene. The compounds chosen were *n*- and *tert.*-butyl alcohols, benzyl alcohol, and diphenylmethanol, and, since behaviour similar to that of the alcohols might be expected with phenol, some measurements on this compound have also been included. As the apparently anomalous P_2 values obtained by some workers for solutions of low concentration could have arisen through the use of incorrect values for the dielectric constant or density of the solvent relative to the values for the solutions, some series of independent measurements have been made upon each of the systems other than that involving benzyl alcohol. In these, four different forms of apparatus have been used to determine the dielectric constants of the solutions relative to that of benzene, and some series of measurements have been extended to very low concentrations of the hydroxylic compounds.

The results have shown that neither the dielectric constants (ε) nor the specific volumes (v) of the solutions vary simply with concentration. Curves were therefore drawn of the variation of ε, v, and the refractive index (n) of the solutions with the weight fraction of solute (w), and from these the values at certain specific concentrations shown in

TABLE 1. *Polarisation and association data for hydroxylic compounds in benzene solution.*

100w	$10^4\Delta\varepsilon$	$10^5\Delta v$	$10^4\Delta n_D$	P_2 (c.c.)	$[R_D]$ (c.c.)	x	100w	$10^4\Delta\varepsilon$	$10^5\Delta v$	$10^4\Delta n_D$	P_2 (c.c.)	$[R_D]$ (c.c.)	x
		n-Butyl alcohol							*tert.*-Butyl alcohol				
0·5	192	65	− 7	81·4	21·8	1·06	0·5	183	101	− 8	80·6	22·5	1·03
1·0	392	128	−13	82·3	22·1	1·12	1·0	367	200	−15	80·5	22·9	1·08
1·5	598	190	−20	83·0	22·0	1·22	1·5	550	297	−23	80·4	22·6	1·16
2·0	809	250	−27	83·5	21·9	1·33	2·0	734	392	−30	80·2	22·8	1·24
2·5	1022	309	−33	83·8	21·9	1·43	2·5	917	485	−38	79·9	22·6	1·33
3·0	1239	368	−39	84·1	22·0	1·53	3·0	1096	576	−45	79·4	22·6	1·40
4·0	1672	483	−52	84·3	21·9	1·74	4·0	1440	754	−60	78·3	22·6	1·56
5·0	2107	595	−64	84·2	22·0	1·91	5·0	1770	929	−75	77·2	22·5	1·71
6·0	2556	710	−75	84·3	22·1	2·07	6·0	2091	1100	−89	76·1	22·5	—
7·5	3262	876	−92	84·6	22·1	2·32	7·0	2411	1270	−103	75·2	22·6	—
					Diphenylmethanol								
0·5	90	−123	5	111·3	57·0	1·00	3·0	558	−738	26	112·5	57·8	1·06
1·0	181	−246	9	111·6	58·1	1·00	4·0	754	−984	34	112·9	57·7	1·11
1·5	273	−369	14	111·8	58·2	1·00	5·0	953	−1230	43	113·2	57·6	1·17
2·0	367	−492	18	112·1	58·0	1·02	6·0	1156	−1476	51	113·5	57·6	—
2·5	462	−615	22	112·3	57·7	1·04	7·0	1361	−1722	—	113·6	—	—
					Phenol								
0·5	131	−112	2	72·0	27·6	—	3·0	870	−672	15	75·8	28·1	—
1·0	267	−224	5	72·7	28·1	—	4·0	1200	−896	20	77·1	28·1	—
1·5	409	−336	7	73·5	27·9	—	5·0	1550	−1120	25	78·3	28·1	—
2·0	558	−448	10	74·4	28·1	—	6·0	1919	−1344	30	79·3	28·1	—
2·5	710	−560	12	75·0	28·0	—	7·0	2306	−1568	35	80·4	28·0	—
					Benzyl alcohol								
1·1340	341	−208	5	91·5	32·5	—	5·6065	1901	−1051	24	96·3	33·0	—
2·5749	817	−483	11	93·9	32·6	—	7·1772	2492	−1353	30	96·7	32·8	—
3·7120	1216	−702	16	95·2	32·7	—	7·6993	2689	−1451	33	96·8	32·7	—
4·6753	1557	−886	20	95·6	32·6	—							

Table 1 were found. The values of P_2 calculated from these figures lie satisfactorily upon the P_2–w curves derived directly from the measurements on the individual solutions.

Table 1 also includes the results of the one series of measurements upon benzyl alcohol. After this had been completed, results for the same temperature were recorded by Buckingham, Holland, and Le Fèvre (*J.*, 1954, 1646). As the agreement between the two

groups of results was remarkably close, no further measurements on this compound were deemed necessary.

To assist in correlating the results with the association of the hydroxylic compounds, cryoscopic measurements have been made on dilute solutions of *n*- and *tert*.-butyl alcohol and of diphenylmethanol in benzene. The cryoscopic constant of benzene being assumed to be 5·2° kg.⁻, the results have been used to evaluate the mean degree of complexity of the alcohol molecules. Interpolated values for various concentrations are shown as x in Table 1 : although these extend beyond the range over which ideal behaviour can be expected. the figures obtained should be of the correct order of magnitude. The results for *n*-butyl alcohol are in fair agreement with the measurements of Giacolone (*Gazzetta*, 1942, **72**, 378).

DISCUSSION OF RESULTS

Wolf and Herold (*Z. phys. Chem.*, 1934, **27**, *B*, 58) pictured the association of two alcohol molecules as occurring in all possible ways ranging between the two extreme configurations (I) and (II) in which the dipoles are parallel and antiparallel, respectively, and they accounted for the variation of P_2 with concentration then reported by supposing the solutions to contain some double and triple molecules with mean dipole moments respectively less and greater than that of a single molecule. On the other hand, Hückel and Schneider (*ibid.*, 1940, **47**, *B*, 227) postulated the existence of two types of double alcohol molecules, approximating to the configurations (I) and (II), steric factors determining which of these predominates in any particular case.

Modern theories of hydrogen bonding render these completely parallel and completely antiparallel arrangements of the dipoles in the associated molecules improbable. To take the simplest possible case, let us suppose that the dipole in the single alcohol molecule acts along the bisector of the C–O–H angle, and that the latter is equal to the tetrahedral angle.
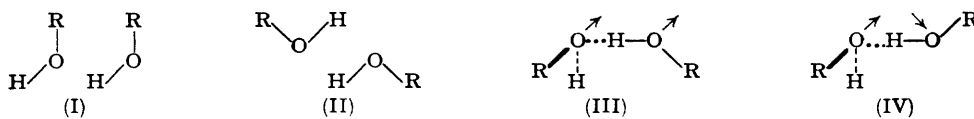
In (III) and (IV) the Bonds O⋯H and R—O are in a plane perpendicular to the paper.

Then, if the two oxygen atoms in a double molecule are collinear with the hydrogen atom bonding them, and rotation is possible about the O–H–O axis, the molecular configurations leading to maximum and minimum resultant moment are those shown in (III) and (IV), respectively. In (III) the dipoles are parallel, and so the moment of the dimer is double that of the monomer, whereas in (IV) the dipoles are inclined at the tetrahedral angle and so the resultant moment is $2/\sqrt{3}$ that of the monomer. The apparent orientation polarisations in the two cases are therefore respectively twice and two-thirds of that of the monomer, so, if rotation is free, P_2 should be increased by the formation of dimeric molecules. If the groups R are bulky, however, as in *tert*.-butyl alcohol, steric factors will cause configurations near to (IV), where the groups R are more remote from one another, to predominate, so the value of P_2 for the dimeric molecules is not likely to be much greater than for the monomeric molecules. Further association to trimeric molecules can lead to configurations with moments ranging from still higher values to nearly zero, but, in the absence of any ordered arrangement, probability considerations make it unlikely that P_2 will attain a very high value. When steric factors enter, adjacent dipoles will be partially opposed, as in (IV), and so P_2 may well fall below the value for the monomeric state. Similar arguments apply when more complex association is involved.

The results for *n*-butyl alcohol indicate that P_2 increases sharply with increasing concentration up to about 2% (w/w), after which it changes less, remaining almost constant between 3 and 6% (w/w). As the value at zero concentration corresponds with the monomeric alcohol, it can be inferred that P_2 is greater for the dimeric than for the monomeric form, as is to be expected if free rotation occurs about the O–H–O axis. The fact that the

increase in P_2 with increasing concentration does not persist much beyond 2% (w/w) suggests that association into more complex forms then becomes appreciable and that this causes no further increase in P_2. In view of these observations it is at first sight rather surprising that the cryoscopic measurements indicate that at a concentration of 2% (w/w) the mean molecular complexity at the freezing point of benzene is 1·33, whilst at 5% it is still only 1·9. At the temperature of the polarisation measurements (25°) the complexity will be lower.

Some light is thrown on this matter, however, by the infrared spectra of carbon tetrachloride solutions of ethyl alcohol, in which the 3638, 3523, and 3300 cm.$^{-1}$ frequencies have been attributed by Errera, Gaspart, and Sack (*J. Chem. Phys.*, 1940, **8**, 63) to the vibrations of hydroxyl groups in single, double, and more highly associated molecules, respectively. Their absorption curves suggest that at 20° the proportion of polymer in 0·125 and 0·25% solutions is small, but that at concentrations of 0·5% and higher, absorption by the polymer exceeds that by the dimer, although the most intense band is still that due to the monomer. If the behaviour of *n*-butyl alcohol follows a similar pattern it seems likely that increase of concentration between 2 and 6% (w/w) is accompanied by an increase in the proportion of polymeric molecules and a decrease in the proportion of monomer, the proportion of dimer only increasing slightly and still remaining relatively small. If P_2 for the polymer is about equal to or slightly less than that of the monomer, such behaviour would account for the course of the P_2–w curve up to about 6% (w/w).

This interpretation suggests that the alcohol tends to exist mainly as monomeric molecules and polymeric aggregates. This is not improbable, since the participation of the hydrogen atom of a hydroxyl group in a hydrogen bond will lead to an increased electron density at the oxygen atom. Hence, steric factors permitting, its chance of becoming "bonded" by the hydrogen atoms of another hydroxyl group should be increased as compared with that of the oxygen atom of a monomeric molecule.

At concentrations above 6% (w/w), P_2 for *n*-butyl alcohol rises again with increasing concentration, and, outside the range studied here, various observers have reported a considerable increase in P_2 between about 10 and 40%, followed by a gradual fall to the value for the pure alcohol. The increase may be due to the establishment of some degree of order in the alcohol aggregates, so that the individual dipoles have less tendency to cancel one another out, whilst the fall in P_2 at very high concentrations can be associated with the inter-linking of the aggregates and consequent hindrance to rotation of the type discussed by Oster and Kirkwood (*J. Chem. Phys.*, 1943, **11**, 175).

In view of the variations of P_2 with concentration, it is interesting that the molecular refraction of *n*-butyl alcohol does not vary appreciably with its extent of association, but remains very close to the value for the pure liquid (22·14 c.c.; Vogel *et al.*, *J.*, 1948, 1817).

At first sight the variation of P_2 with concentration for benzene solutions of *tert.*-butyl alcohol seems very different from that for solutions of *n*-butyl alcohol. P_2 remains almost constant up to about 2% (w/w) of alcohol, and then decreases gradually with increasing concentration. The cryoscopic measurements indicate that over the concentration range studied *tert.*-butyl alcohol is only slightly less associated than is the *n*-isomer. The analogy between the behaviour of the two compounds becomes clear, however, if it is assumed that, owing to steric factors, the dimer of *tert.*-butyl alcohol has a mean P_2 value approximately equal to that of the monomer, but that further increase in complexity leads to a decrease in P_2.

Both for *n*- and for *tert.*-butyl alcohol the specific-volume determinations indicate that the partial molar volumes of the alcohols decrease with increasing concentration. In each case this decrease is most rapid at concentrations below 2% (w/w), the values at the highest concentrations studied being only slightly higher than for the pure liquids.

For the other three solutes studied the variations of P_2 with concentration are similar in type but differ in degree. In each case P_2 increases with increasing concentration but the rate of change becomes progressively less the greater the concentration. The cryoscopic measurements indicate that diphenylmethanol is much less associated in benzene solution than is either *n*- or *tert.*-butyl alcohol at similar concentrations. As in this case the increase of P_2 with increasing w is only small, the polarisation results can be explained by

supposing that P_2 is appreciably higher for dimeric molecules than for the monomer, but that further increases in complexity have little effect on P_2.

Although the sharp rise in the P_2–w curves for benzyl alcohol and phenol suggests that the greatest increase in P_2 occurs on passing from monomeric to dimeric molecules, the fact that P_2 continues to increase with increasing w over the whole concentration range studied makes it probable that for these compounds the mean value of P_2 for the polymeric molecules may always be greater than for the monomer. The difference between this behaviour and that of the butyl alcohols indicates the possibility that the presence of the aromatic ring may induce some degree of order in the aggregates even at relatively low concentrations.

The curvature of the P_2–w and ε–w plots for all the systems studied, and of the v–w plots for n- and *tert.*-butyl alcohol, renders the extrapolation of these results to zero concentration less exact than for most solutes. The number of series of measurements carried out, however, has made possible a fairly accurate estimate of the gradients of these curves at zero concentration, and from these the dipole moments of the monomeric molecules in benzene solution have been derived. The results are shown in Table 2, together with the

TABLE 2. *Dipole moments in benzene solution.*

	α	β	ν	$P_{2\infty}$ (c.c.)	$[R_D]_2$ (c.c.)	μ (D)	Previous values
n-Butyl alcohol	3·77	0·133	−0·40	80·7	22·0	1·69	1·62—1·74 [a]
tert.-Butyl alcohol ...	3·65	0·206	−0·44	80·7	22·6	1·69	1·55—1·66 [a]
Diphenylmethanol ...	1·78	−0·246	0·27	110·8	57·7	1·62	1·64 [b]
Benzyl alcohol	2·90	−0·188	0·12	89·8	32·7	1·67	1·68—1·69 [a] 1·67₅ [c]
Phenol	2·55	−0·224	0·15	71·0	28·0	1·45	1·5—1·7 [a]

α, β, and ν are the limiting values, at zero concentration, of $\delta\varepsilon/\delta w$, $\delta v/\delta w$, and $\delta n^2/\delta w$, respectively. References : [a] Weedon, "Massachusetts Institute of Technology Tables," Technology Press, Cambridge, Mass., 1948; [b] Cleverdon and Smith, *J.*, 1951, 2321; [c] Buckingham, Holland, and Le Fèvre, *J.*, 1954, 1646.

parameters from which they have been computed and indications of the ranges covered by previous values for benzene solutions. The wide variation of the moments previously reported for n- and *tert.*-butyl alcohol reflects the varied interpretations of measurements on solutions of low concentration. The moment for diphenylmethanol previously recorded was slightly higher than that now reported because it was erroneously supposed that $\Delta\varepsilon/w$ and P_2 were approximately linear with w. The value now found for phenol in benzene is appreciably lower than has previously been reported, principally because the rapid fall of P_2 with decreasing concentration seems to have been largely neglected in the earlier evaluations. The new value, however, falls much better into line with the moment for the vapour (1·40 D; Groves and Sugden, *J.*, 1937, 1782), particularly as the dipole moment of anisole appears to be *lower* in benzene solution than in the vapour.

EXPERIMENTAL

Materials.—Benzene was purified and dried as described by Few and Smith (*J.*, 1949, 753). "Laboratory reagent" n- and *tert.*-butyl alcohol were refluxed for 3 hr. over freshly ignited calcium oxide and then further refluxed for some hours over calcium metal. They were finally distilled through a 20-plate column under anhydrous conditions. Different batches had closely concordant physical properties. n-Butyl alcohol had b. p. 117·8°/760 mm., d_4^{25} 0·80575, n_D^{25} 1·3973—1·3974 (Timmermans, "Physical Constants of Pure Organic Compounds," Elsevier, New York, 1950, gives b. p. 117·8—118·0°/760 mm., d_4^{25} 0·80567—0·80572, n_D^{25} 1·3970—1·3974). *tert.*-Butyl alcohol had m. p. 25·54°, b. p. 82·5°/763 mm., d_4^{25} 0·7811, n_D^{25} 1·3851 (Timmermans, *op. cit.*, gives b. p. 82·45°/760 mm., and interpolation of his data leads to d_4^{25} 0·7814, n_D^{25} 1·3851). "Laboratory reagent" benzyl alcohol was redistilled twice, the middle fraction being retained in each distillation. The sample used had b. p. 203·5°/748 mm., d_4^{25} 1·04157, n_D^{25} 1·5375 (Timmermans gives b. p. 205·25—205·45°/760 mm., d_4^{25} 1·04156). "Laboratory reagent" diphenylmethanol was recrystallised several times from petrol (b. p. 60—80°) and stored over phosphoric oxide : it had m. p. 66·4°. "Separate crystal" phenol was distilled twice at atm.

pressure, the initial fractions being rejected, and was used immediately; it had b. p. 182°/763 mm. (Timmermans gives b. p. 181·75—182·2°/760 mm.).

Apparatus and Methods.—A few of the earlier dielectric constant measurements were carried out with an apparatus similar to that described by Le Fèvre and Rayner (*J.*, 1938, 1921), and the remainder with the resonance apparatus and two forms of the heterodyne heat apparatus described by Few, Smith, and Witten (*Trans. Faraday Soc.*, 1952, **48**, 211). Specific volumes were determined with pyknometers of 8—10 c.c. capacity. Some of the refractive indices were determined with a Pulfrich refractometer and the remainder with an Abbé refractometer. All these measurements were made at 25·0°.

Cryoscopic measurements were made in an apparatus of the Beckmann type, through which a stream of dry nitrogen, saturated with the vapour of benzene at its m. p., was circulated