CCCLXX.—*The Dielectric Constants of Mixtures of Organic Liquids.*

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PREVIOUS investigations of the dielectric constants of mixtures of two organic liquids carried out with the object of finding a suitable mixture formula (Silberstein, *Wied. Ann.*, 1895, **56**, 661; Linebarger, *Z. physikal. Chem.*, 1896, **20**, 131; Philip, *ibid.*, 1897, **24**, 18; Dobroserdov, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 679; Grützmacher, *Z. Physik*, 1924, **28**, 342) have paid little attention to other changes which are known to occur on mixing. The simplest of the suggested formulæ is the volumetric rule of Silberstein (*loc. cit.*), *viz.*, $\varepsilon = (\varepsilon_1 v_1 + \varepsilon_2 v_2)/(v_1 + v_2)$, where ε, ε_1, ε_2 are the *D.C.*'s of the mixture and of the two components, respectively, and v_1 and v_2 are the volumes of the two components. This rule results from the definition of the *D.C.* as a property referring to equal volumes of different substances; accordingly, when two liquids are mixed, if it is assumed (1) that the dielectric properties of the two kinds of molecules remain the same as before mixing, and (2) that the respective molecules retain the same volume in the mixture as in the pure state, it follows that the *D.C.* of the mixture should be given by Silberstein's equation. Dobroserdov investigated a large number of organic mixtures; for several of these approximate agreement was obtained with this rule, but others showed marked deviations. The explanation of these divergences was that chemical compounds were formed between the components of the mixtures, but as in most cases one component was an inert liquid such as benzene, heptane, or carbon tetrachloride, this explanation is scarcely acceptable. Changes in the number of molecules may be caused, however, not only through combination taking place between the two components, but also through changes in the degree of association of one or both. In addition, it is also necessary to consider changes of a more physical nature such as have been discussed by Hildebrand (*J. Amer. Chem. Soc.*, 1916, **38**, 1458), *i.e.*, those due to the different environment of the molecules in the mixture from that in the pure state. It appears possible that such changes may be the cause of the deviations noted and, with the object of testing further the validity of the volumetric rule and of ascertaining to what extent deviations from it can be explained in this way, a number of mixtures consisting of benzene as one component and a benzene derivative as the other were investigated.

EXPERIMENTAL.

Method of Determination of Dielectric Constant.—By the use of the thermionic valve an apparatus was constructed for which great accuracy is not claimed, but by means of which the *D.C.* can be determined rapidly and with sufficient accuracy for the present purpose. The actual experimental arrangement is based on a method described by Jackson (*Phil. Mag.*, 1922, **43**, 482) and is similar to that used by Grützmacher (*loc. cit.*). The method gave consistent results as exemplified by those for benzene at 15° ± 1°: $\varepsilon = 2{\cdot}28, 2{\cdot}28, 2{\cdot}27, 2{\cdot}29, 2{\cdot}26, 2{\cdot}28, 2{\cdot}27, 2{\cdot}27$: mean, 2·28. After correction for difference of temperature, this value compares favourably with those obtained at 25° by Graffunder (2·268; *Ann. Physik*, 1923, **70**, 225), Grützmacher (2·278; *loc. cit.*), and Isnardi (2·268; *ibid.*, 1922, **9**, 153), but it is rather higher than those given by Sayce and Briscoe (J., 1925, **127**, 315) and by Harris (*ibid.*, p. 1065).

The wave-length used throughout this investigation was 95 metres, *i.e.*, a frequency of approximately 3×10^6 cycles per second.

The results are in Table I: under "Comp." is the composition of the mixture in terms of the percentage by volume of the component other than benzene; ε (obs.) are the values of the *D.C.* determined; and "Diff." denotes the deviations from the values calculated from the volume rule. The mixtures were made up by measuring the required volumes by pipettes and checking by weight. The variation of temperature was not more than 0·5° throughout each series. The liquids used were dried over suitable reagents and fractionally distilled until a constant-boiling fraction (within a range of 0·2°) was obtained.

Table I.

	Methyl benzoate (12°).		Ethyl benzoate (15°).		Phenetole (15°).		Ethyl cinnamate (16°).	
Comp.	ε (obs.).	Diff.	ε (obs.).	Diff.	ε (obs.).	Diff.	ε (obs.).	Diff.
0	2·28	—	2·28	—	2·28	—	2·28	—
20	3·18	+0·01	3·09	+0·04	2·63	−0·05	3·03	+0·05
40	4·04	−0·02	3·85	+0·03	3·12	+0·01	3·74	+0·05
60	4·93	−0·01	4·59	+0·01	3·53	−0·01	4·42	+0·02
80	5·82	−0·01	5·32	−0·03	3·95	±0·00	5·14	+0·02
100	6·72	—	6·12	—	4·37	—	5·83	—
	Dimethylaniline (14°).		Chlorobenzene (15°).		Bromobenzene (16°).		Aniline (14°).	
0	2·28	—	2·27	—	2·28	—	2·28	—
5	2·51	+0·09	2·47	+0·03	—	—	—	—
10	2·65	+0·09	2·62	+0·01	2·65	+0·05	—	—
15	2·83	+0·14	2·88	+0·10	—	—	—	—
20	3·02	+0·19	3·04	+0·09	2·99	+0·07	3·16	−0·11
40	3·52	+0·13	—	—	3·60	+0·05	4·05	−0·21
50	—	—	4·04	+0·07	—	—	—	—
60	4·07	+0·13	—	—	4·21	+0·02	5·02	−0·24
80	4·63	+0·13	4·99	±0·00	4·81	−0·01	6·07	−0·19
100	5·05	—	5·67	—	5·46	—	7·20	—
	Benzaldehyde (15°).		Nitrobenzene (15°).		Benzyl alcohol (14°).		*m*-Cresol (16°).	
0	2·28	—	2·28	—	2·28	—	2·28	—
20	4·81	−0·63	6·74	−2·49	3·37	−1·18	3·28	−1·13
40	7·46	−1·13	11·90	−3·48	4·86	−1·86	4·82	−1·73
60	10·57	−1·28	18·19	−3·74	7·46	−1·63	6·95	−1·73
80	13·92	−0·99	25·81	−2·67	10·58	−0·78	9·86	−0·96
100	18·07	—	35·03	—	13·63	—	12·95	—

Discussion of Benzene Mixtures.

A number of these mixtures obey the volumetric rule fairly accurately. On the other hand, marked deviations are obtained for the mixtures of benzene with aniline, benzaldehyde, *m*-cresol, benzyl alcohol, or nitrobenzene, which have curves (*D.C.*–volumetric composition) convex to the axis of concentration to a varying extent. These substances, however, all show association in benzene solution (Turner, "Molecular Association," Appendix), and thus a simple explanation is available for the divergences of these mixtures. According to Debye's theory of dielectrics (*Physikal. Z.*, 1912, **13**, 97), molecules possess permanent dipoles. When two molecules associate, the new complex has a different moment and, if it be assumed that the association takes place so that the net effect is a partial neutralisation of the moments of the individual dipoles, this moment will be smaller than the sum of the original moments, thus causing a fall in the dielectric properties of the substance. As those substances which have normal molecular weights in benzene give linear curves for the *D.C.* when mixed with that solvent, we can safely attribute the marked divergences of the mixtures of benzene with aniline, benzaldehyde, nitrobenzene, benzyl alcohol, or *m*-cresol to the association known to occur in the mixtures.

With several mixtures, there is a deviation from the straight line which, although slight, is of the same nature for each mixture. The best example is benzene–dimethylaniline, but similar deviations obtain for chloro- and bromo-benzene with benzene and to a less marked degree for benzene–ethyl cinnamate. The values of the *D.C.*'s for these mixtures are all slightly greater than those required by the volume rule and the deviations are greatest at low concentrations of the benzene derivative : the corresponding curves are approximately linear down to concentrations of about 20%, but after that point they show a distinct drop. Although these deviations are very slight, the fact that they occur in the same manner for several mixtures seems to testify to their actual existence and requires an explanation.

Only changes in the degree of association have up till now been considered. As mentioned above, however, the physical effect of the difference of the cohesive forces acting on the molecules in the mixture also requires attention; in previous discussions of the *D.C.*'s of mixtures differences of this nature have been ignored. When a liquid is subjected to an alternating electric field, as when the *D.C.* is determined, the molecules may be considered to be maintained in a state of rapid vibration (Debye, *Verh. deut. physikal. Ges.*, 1913, **15**, 777); the amount of this vibration depends partly on the strength of the external field, the size of the dipoles, and the heat motions of the molecules, but also on the cohesive forces between neighbouring molecules. These forces will not in general be the same in a mixture as in the component substances, and the amplitude with which a molecule vibrates for a given external field will undergo a slight change on mixing : this will have an effect on the dielectric action of the molecules. Thus, if the cohesive forces acting in a liquid A are smaller than those in a liquid B, then, when A and B are mixed, the forces acting on B molecules will be smaller in the mixture than in B itself and, accordingly, the molecules will have a greater freedom of vibration, thus causing the contribution which they make to the dielectric action of the mixture to be larger than predicted by the mixture rule. Such effects should be greatest at low concentrations, and the greatest divergences for the *D.C.*'s of the mixtures under consideration occur also at low concentration.

The internal pressure as calculated by Hildebrand (*loc. cit.*) is the only available measure of these cohesive forces in the liquid state, and with the object of testing the above hypothesis the relative internal pressures (π) for these substances have been calculated from surface tension data (Landolt-Börnstein's Tabellen). The formula used was $\pi = \gamma/v^{1/3}$, where γ and v are the surface tension and molecular volume, respectively, and the values are in Table II.

TABLE II.

Relative Internal Pressures at 20°.

Benzene	6·54	Chlorobenzene	7·05
Ethyl benzoate	6·61	Bromobenzene	7·50
Methyl benzoate	(7·44)	Dimethylaniline	7·28
Phenetole	6·46	Ethyl cinnamate	6·73

According to this explanation, the internal pressures of those substances the mixtures of which with benzene have abnormally high values of the *D.C.* should be greater than that of benzene, whereas those substances which obey the volumetric rule accurately in benzene solution should have internal pressures approximately equal to that of benzene. Table II shows that this is actually the case with the single exception of methyl benzoate: chlorobenzene, bromobenzene, and dimethylaniline all have values decidedly higher than benzene, and ethyl cinnamate, the mixture of which with benzene shows only a slight deviation, occupies an intermediate position with a value only slightly greater than that for benzene; ethyl benzoate and phenetole, on the other hand, have values approximately equal to that for benzene. The internal pressure calculated for methyl benzoate seems anomalous when compared with that of ethyl benzoate, for the two esters resemble each other closely in other properties, both in the pure state and in mixtures; it appears quite possible, therefore, that the value calculated for methyl benzoate is based on incorrect data. With this single doubtful exception, then, these figures indicate that those mixtures, of which the two components have nearly equal internal pressures and therefore approach closely to ideal solutions, obey the simple volumetric mixture rule, and, further, that internal pressure differences between the two components of a non-associating mixture cause slight deviations from this rule.

The foregoing considerations show that both chemical and physical changes on mixing must be taken into account in discussing the dielectric constants of mixtures. For polar substances, Hildebrand (*loc. cit.*, p. 1461) states that the former effects outweigh the latter, and this is evident from those mixtures in which association occurred. It is possible, however, that at low dilutions, where the physical effects are greatest, such changes may cause quite an appreciable effect even with polar substances. Partington and Rule (*Phil. Mag.*, 1926, **1**, 1035) have investigated a number of dilute solutions of organic solids and observe that for benzene–benzoic acid the *D.C.* increases with concentration to a maximum at about 1% concentration and then decreases; no explanation was brought forward for this behaviour, and it is now suggested that this is an example of physical changes causing an appreciable effect at low concentrations but becoming negligible in comparison with association changes at higher concentrations.

Mixtures containing Ether as One Component.

In the benzene mixtures no case has been obtained where the *D.C.* of the mixture is much higher than that required by the volume rule. Dobroserdov (*loc. cit.*), however, describes a number of mixtures which have curves concave to the axis of concentration and show marked deviations, *e.g.*, with ether–chloroform (compare Philip, *Z. physikal. Chem.*, 1897, **24**, 18) the *D.C.* attains a maximum value higher than that of either component. These mixtures all contain an ether as one component and, in order to enquire further into their nature, a number of mixtures of ethyl ether with benzene derivatives have been examined: the results are in Table III, "Comp." denoting the volume percentage of the component other than ether.

TABLE III.

	Dimethylaniline (17°).		Benzaldehyde (18°).		*m*-Cresol (17°).	
Comp.	ϵ (obs.).	Diff.	ϵ (obs.).	Diff.	ϵ (obs.).	Diff.
0	4·40	—	4·35	—	4·41	—
20	4·56	+0·03	6·97	−0·03	5·94	−0·24
40	4·65	−0·01	9·65	±0·00	7·49	−0·30
60	4·80	+0·02	12·38	+0·09	9·15	−0·33
80	4·90	−0·01	15·01	+0·07	11·00	−0·16
100	5·04	—	17·59	—	12·85	—
	Nitrobenzene (20°).		Chlorobenzene (15°).		Aniline (15°).	
0	4·35	—	4·46	—	4·44	—
20	9·51	−0·75	4·79	+0·08	5·58	+0·62
40	15·07	−1·10	5·06	+0·10	6·30	+0·82
60	20·88	−2·21	5·37	+0·17	6·70	+0·70
80	27·26	−0·74	5·58	+0·13	6·98	+0·46
100	33·91	—	5·70	—	7·04	—

In the above series there are again instances of mixtures which obey the volumetric mixture rule fairly accurately; from what has been proved for the benzene series these mixtures—ether with benzaldehyde and with dimethylaniline—can be accepted as normal and the deviations of the others from this rule must be attributed to changes on mixing. Two mixtures—ether with *m*-cresol and with nitrobenzene—have curves deviating only slightly from the straight line with values smaller than those required. This is in good accord with the association changes discussed for the benzene series, and with the fact that polar substances which have abnormal molecular weights in inert solvents give practically normal values in ether (Turner, *op. cit.*); the slight deviations show that association still takes place, but to a much smaller extent, causing the observed lowering of *D.C.* The remaining mixtures—with aniline or chlorobenzene—have curves concave to the axis of concentration and resemble those described by Dobroserdov. The difference between these two mixtures and the other four cannot be attributed to differences of internal pressure, since all the liquids mixed with ether in this series are alike in having much higher internal pressures than ether. It appears, therefore, that some chemical explanation must be sought.

In the discussion of benzene mixtures, the only type of association product considered was that which caused a partial neutralisation of the moments of the participating molecules, *i.e.*, the dipoles joined laterally; Ebert (*Z. physikal. Chem.*, 1924, **113**, 1), however, suggests that another type is possible in which the dipoles join end-on. This association gives a product with a moment equal to the sum of the moments of the participating dipoles, but, as the polarisation produced is proportional to the square of the moment of the dipole (Lange, *Z. Physik*, 1925, **33**, 169), the net effect is to cause an increase of the dielectric properties and not a decrease as with the association previously considered. The nature of the association product formed is determined by the sizes of the dipoles and their geometrical positions in the participating molecules. If association takes place between molecules of the same kind, the two dipoles, being of the same size, will be able to fit easily together, giving association of the first type and causing a fall of *D.C.* as found with substances associating in benzene solution. Association, however, may also take place between molecules of different substances and, when this occurs, there may be considerable differences in the sizes of the molecules and in the geometrical positions of the dipoles in the molecules. In consequence, the dipoles are not able to fit together in the above manner, but, instead, they may join end-on, giving association of the second type which produces a rise in dielectric properties. The most suitable conditions for this kind of association obtain with the mixtures under discussion, for ether has a small molecule compared with the benzene derivatives, and the sizes of the dipoles in the two molecules will be quite different. A simple explanation of the abnormally high values of the *D.C.* obtained in some cases is thus afforded by association of this kind.

It appeared of interest to obtain further evidence that these different kinds of association can take place from mixtures of liquids which would be expected, from chemical evidence, to show some tendency to combine. Mixtures of aniline–*m*-cresol and of acetone–chloroform (which under certain conditions form a compound) were therefore investigated; the results are in Table IV, from which it is seen that these two mixtures behave in quite different manners, the acetone–chloroform mixture having higher and *m*-cresol–aniline lower values than required by the mixture rule. This suggests that the two different kinds of association to which reference has been made are occurring in these mixtures, the second type taking place in the former and the first type in the latter case. This is in good agreement with the conditions already mentioned for formation of the two kinds. In *m*-cresol and aniline, the molecules are of nearly the same size and accordingly fit together easily, giving association of the first type; on the other hand, acetone and chloroform have molecules bearing no relationship to each other in structure and thus, since the dipoles are of different sizes, association of the second type takes place. These results, therefore, support the view that different kinds of products can be formed when association takes place and that the nature of the product formed depends on the relative sizes and shapes of the dipoles in the participating molecules.

TABLE IV.

Acetone–Chloroform (17°).			*m*-Cresol–Aniline (17°).		
Comp.	ϵ (obs.).	Diff.	Comp.	ϵ (obs.).	Diff.
0	4·85	—	0	7·04	—
20	9·37	+1·31	20	7·87	−0·36
40	12·84	+1·57	40	8·62	−0·80
60	15·67	+1·20	50	9·03	−0·98
80	18·32	+0·64	60	9·47	−1·13
100	20·89	—	80	10·45	−1·34
			100	12·98	—

Summary.

The dielectric constants of a number of mixtures of benzene derivatives with benzene have been determined. Those mixtures which approach most closely to ideal solutions obey the simple volumetric-mixture rule. Differences in internal pressure between the components of non-associating mixtures cause slight deviations

from this rule. Association taking place in these mixtures causes a lowering of dielectric properties. A number of mixtures of benzene derivatives with ether have also been examined, and with some of these the dielectric constants are considerably greater than those required by the volumetric rule. From these results it is concluded that the effect of association on the dielectric constant depends on the nature of the complex formed, and this is determined by the sizes and shapes of the participating dipoles. This view is supported by results obtained with acetone–chloroform and *m*-cresol–aniline mixtures.

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