CCCXLIV.—*The Dielectric Constants of Some Liquids and Liquid Mixtures.*

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IN the course of an investigation into the nature of solution it became necessary to examine the physical properties of a number of binary mixtures of organic liquids. Amongst other properties, the dielectric constants of such mixtures came under review. A certain amount of data had already been placed upon record (Linebarger, *Z. physikal. Chem.*, 1896, **20**, 130; Philip, *ibid.*, 1897, **24**, 18; Schultze, *Z. Elektrochem.*, 1912, **18**, 77), but it seemed desirable to examine particularly certain pairs of liquids the admixture of which had been observed to be attended by interesting changes in temperature and in density. It is here proposed to give an account of the method of measurement and the results obtained; a discussion of these results in their relation to other physical properties is deferred until further data are available.

The method of measurement was substantially that previously described (Sayce and Briscoe, J., 1925, **127**, 315; Sayce, *J. Scient. Instr.*, 1926, **3**, 116), but improvements have been made in the apparatus which add much to its convenience and speed of operation. Thus, both the galvanometer scale and the scale of the condenser C_V (J., *loc. cit.*) have been brought into the field of vision of the reading telescope and the movements of both the oscillator condenser C_2 and the condenser C_V are now controlled by dials permitting of extremely fine adjustment. Errors due to sudden variations of atmospheric temperature are minimised by enclosing C_V and the bank of condensers, C_a to C_t, in wooden boxes lined with stout copper, and the inconvenience of working in a darkened thermostatic laboratory has thus been removed except in determinations of the utmost precision.

In the present case, it was considered unnecessary to make use of the full accuracy of which the method was capable; therefore an economy of dielectric and a saving of time were effected by the use of a much smaller dielectric container, which took the form

FIG. 1.

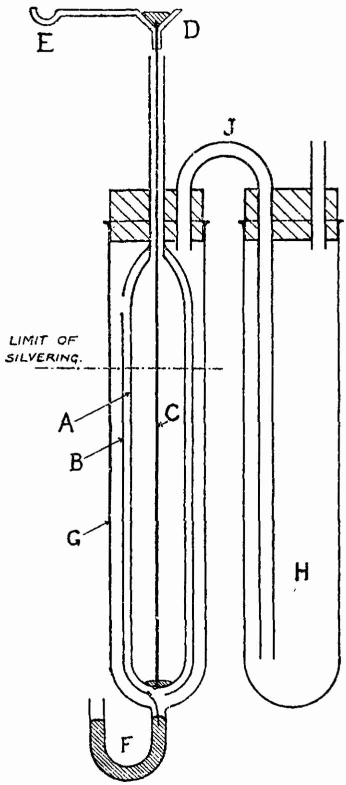
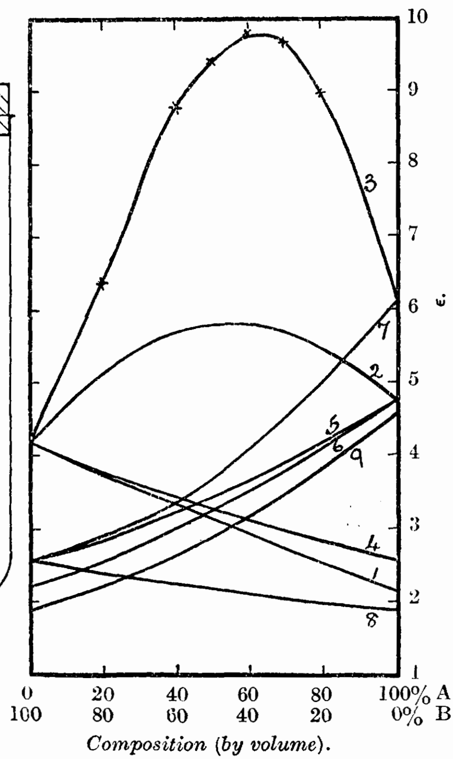


FIG. 2.



shown in Fig. 1. The condenser proper consisted of silver coatings upon two tubes, *A* and *B*, welded together at the top and separated by an annular space of approximately 1 mm. Electrical contact was made with the inner coating by means of a platinum seal in the tip of *A*, to which a stiff copper wire, *C*, was connected by a globule of mercury. A glass cup, *D*, containing mercury, was cemented to the top of *C* and provided the means of connecting the inner coating of the condenser to the "live" side of the measuring apparatus by transferring a stiff copper wire from the glass rest, *E*, to the mercury in *D*. The condenser was contained in an outer jacket, *G*, having a U-tube, *F*: a platinum wire sealed into *B* and dipping into this mercury in *F* served to make electrical connexion between the silver coating of *B* and the earthed side of the measuring apparatus. A second vessel, *H*, similar to *G* and initially containing the liquid dielectric under examination, was connected to it by the tube *J*, and the whole apparatus was almost completely immersed in a thermostat.

The measurement of the dielectric constant of a liquid or liquid mixture involved the following operations:

1. 50 C.c. of the given dielectric were placed in *H*, which was then closed by a cork and drying-tube.

2. The condensers of the measuring apparatus were inter-calibrated.

3. The capacity of the dielectric container filled with air, C_{air}, was measured.

4. The contents of *H* were blown over into *G*. (The cork which closed *G* was provided with a channel to allow the displaced air to escape.)

5. The capacity of the dielectric container filled with the given dielectric, $C_{\text{liq.}}$, was measured.

The dielectric constant of the liquid was (subject to a correction to be discussed hereafter) given by the ratio $C_{\text{liq.}}/C_{\text{air}}$ (to the standard $\varepsilon_{\text{air}} = 1$).

The apparatus when first used gave results subject to a troublesome inconsistency. The value of the *D.C.* of a liquid when measured with the full accuracy of the method differed from that measured in the manner described above. The reason for this inconsistency may also account for some of the grave irregularities which are evident on comparing the values of the dielectric constants determined by various workers. The *D.C.* of a liquid is actually equal to the ratio $C_{\text{liq.}}/C_{\text{air}}$ only when the capacity of the dielectric container is due entirely to "replaceable" dielectric; *i.e.*, air or the liquid under examination. In practice, however, it is found impossible to eliminate entirely a small "residual" capacity due to that between the lead *C* and the earthed portions of the apparatus. This residual capacity is, in every measurement, added to that due to the liquid or air, respectively, and produces an error which increases with the *D.C.* of the liquid. Thus the capacity due to the liquid is not the measured value, $C_{\text{liq.}}$, but a smaller value $(C_{\text{liq.}} - X)$, where X is the residual capacity. Similarly, the capacity due to the replaced air is not the measured value, C_{air}, but $(C_{air} - X)$. It is evident, therefore, that the true value of the *D.C.* is $(C_{liq.} - X)/(C_{air} - X)$. When, however, the dielectric container is itself of large capacity and of the form shown in the former paper (Fig. 2, J., *loc. cit.*), X becomes extremely small in proportion to the total capacity and may usually be disregarded. In the latter circumstances, the *D.C.* of a certain sample of ether was found to be 4·1140, but when measured in the condenser described above, the value of $C_{liq.}/C_{air}$ at the same temperature was 3·95. The replacement of the water in the thermostat by paraffin oil and the use of a glass instead of a metal vessel for containing the thermostatic liquid diminished the residual capacity considerably and increased the value of $C_{liq.}/C_{air}$ to 22394/5528 = 4·05. Assuming that 4·1140 was the true *D.C.* of the ether sample, the value of X was taken as $\dfrac{\varepsilon C_{air} - C_{liq.}}{\varepsilon - 1}$* $= \dfrac{(4{\cdot}1140 \times 5528) - 22394}{3{\cdot}114}$ = 105 arbitrary units (= 0·7 micro-microfarad approx.). This value was applied as a correction to all the results here recorded. Each determination was performed in duplicate and no result was accepted unless the duplicate determinations were concordant.

Finally, the dielectric constants of a number of binary mixtures were examined in various proportions. For every determination shown in Table II sufficient of the two liquids to make 50 c.c. of the mixture was measured out from burettes.

TABLE I.

Dielectric Constants of Organic Liquids.

Temperature 25°. Frequency, $10^6 \sim$ per second (approx.).

	ϵ.		ϵ.
Benzene	2·23	Pentachloroethane	3·60
Toluene	2·33	Monochlorobenzene	5·44
Hexane	1·89	Dichlorobenzene	7·47
Ether (diethyl)	4·21	Ethylene dibromide	4·70
Carbon disulphide	2·58	*o*-Chlorophenol	6·31
Chloroform	4·79	Phenyl acetate	5·15
Bromoform	4·73	*iso*Butyl acetate	5·32
Carbon tetrachloride	2·20	Amyl acetate	4·62
Tetrachloroethane	7·83		

Results.

The dielectric constants of seventeen organic liquids, as measured by the above method, are recorded in Table I. The small but appreciable conductivity of a number of liquids, including the lower alcohols, acetates, oxalates, acetone, etc., prevented our

* $\epsilon = \dfrac{C_{liq.} - X}{C_{air} - X}$, $\epsilon C_{air} - \epsilon X = C_{liq.} - X$, $X = \dfrac{\epsilon C_{air} - C_{liq.}}{\epsilon - 1}$.

obtaining trustworthy measurements in such cases. It appears to us, however, that the dielectric constant of a substance containing an unknown number of free ions is, in any case, of little significance. Most of the liquids examined were of the B.D.H. " A.R." grade.

The results obtained for nine binary mixtures of organic liquids are set out in Table II and Fig. 2.

TABLE II.

Dielectric Constants of Binary Mixtures.

Temperature 25°. Frequency, 10^6 ~ per second (approx.).

Mixture.	Graph and mixture No.	Mixture.	Graph and mixture No.
A. Carbon tetrachloride.	1	A. Chloroform.	6
B. Ether (diethyl).		B. Carbon tetrachloride.	
A. Chloroform.	2	A. *o*-Chlorophenol.	7
B. Ether (diethyl).		B. Carbon disulphide.	
A. *o*-Chlorophenol.	3	A. Hexane.	8
B. Ether (diethyl).		B. Carbon disulphide.	
A. Carbon disulphide.	4	A. Ethylene dibromide.	9
B. Ether (diethyl).		B. Hexane.	
A. Chloroform.	5		
B. Carbon disulphide.			

% A (by volume).	Mixture No.								
	1.	2.	3.	4.	5.	6.	7.	8.	9.
0	4·21	4·21	4·21	4·21	2·58	2·20	2·58	2·58	1·89
10	3·99	4·69	—	—	—	—	—	—	—
20	3·78	5·13	6·37	3·79	2·89	2·59	2·90	2·42	2·22
30	3·56	5·47	—	—	—	—	—	—	—
40	3·36	5·70	8·77	3·45	3·28	3·04	3·42	2·28	2·66
50	3·15	5·82	9·41	—	—	—	—	—	—
60	2·94	5·79	9·82	3·13	3·71	3·56	4·14	2·12	3·21
70	2·75	5·67	9·68	—	—	—	—	—	—
80	2·56	5·44	8·93	2·84	4·21	4·14	5·08	2·02	3·88
90	2·36	5·13	—	—	—	—	—	—	—
100	2·20	4·79	6·21	2·58	4·79	4·79	6·21	1·89	4·63

We desire to acknowledge a grant from the Department of Scientific and Industrial Research which enabled one of us (L. A. S.) to take part in this investigation.

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NEWCASTLE-UPON-TYNE. [*Received, August* 13*th*, 1926.]