ON THE ANOMALOUS DISPERSION AND ABSORPTION OF ELECTRIC WAVES. II.⁽¹⁾

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Received March 24, 1926. Published May 28, 1926.

As the result of the preliminary experiment it was found that several alcohols, monovalent as well as polyvalent, show anomalous dispersions of the electric wave of 6.1 meters accompanied by anomalous absorptions.⁽²⁾ Similar experiments were carried out with the wave of 9.5 meters. In this case the values of the dielectric constants were calculated introducing proper corrections to direct observations. Also the values of anomalous absorptions were expressed in terms of electric conductivities which are equivalent to them.

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(1) Read before the Chemical Society of Japan, April 5, 1926.

(2) This journal, **1** (1926), 47.

The oscillating circuit as well as the resonating are quite similar to that used in the case of the wave of 6.1 meters. Fig. 1 shows the resonating circuit.

Measurement of Absorption. If the substance under investigation is non-absorbent, the value I/I_0 (I and I_0 being the deflections of the galvanometer G at the resonance when X is filled with the substance and the air respectively) is always unity, provided that the inductance of the leading wires from C to X is very small. If the substance is an absorbent, I/I_0 is necessarily less than unity, and depends upon the electric capacity of X. To find the expression of the anomalous absorption depending only upon the characteristics of each substance this is replaced by an equivalent normal absorption (*i.e.* an absorption which is caused only by the electric conductivity), and the specific conductivity of the latter is taken as the measure of the former.

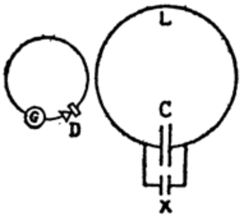

Fig. 1.

A series of experiments showed first of all that water and acetone do not absorb the wave of 9.5 meters and secondly that when the salts such as NaCl, KI, etc. are dissolved in them, the value of I/I_0 depends almost only upon the electric conductivity of the solution. For example the acetone solution of KI and the aqueous solution of NaCl, having the same conductivity, show the same value of I/I_0. These solutions can be used, therefore, as the standards to compare the two kinds of absorptions. The values I/I_0 with respect to corresponding electric conductivities were measured with the acetone solution of KI and the result is shown in Table 1.

TABLE 1.

Approximate Dilution of KI mol per litre	Specific Conductivity cm^{-1} ohm^{-1}	I/I_0 Vessel I	I/I_0 Vessel II	I/I_0 Vessel III	I/I_0 Vessel IV
240	48×10^{-5}	0.04	0.03	—	—
480	26×10^{-5}	0.08	0.06	0.05	0.04
960	14×10^{-5}	0.16	0.12	0.10	0.09
1920	7×10^{-5}	0.28	0.22	0.19	0.18
3840	3.5×10^{-5}	0.48	0.38	0.35	0.34
7680	1.8×10^{-5}	0.66	0.57	0.55	0.55

Measurement of Dielectric Constant. The value of the dielectric constant ε of a non-absorbent can be obtained from the displacement ΔC of the glass plate of the variable capacity C (Fig. 1). But if the substance is an absorbent, ΔC corresponds to a capacity shunted by a conductivity. Therefore to calculate the value of ε of such a substance from ΔC, the correction which corresponds to this conductivity should be known. In the present experiment the following method was adopted.

Recently Walden(1) studied the change of the dielectric constant between a pure solvent and a solution obtained by dissolving a salt in it, and found that the change is less than a few percent for an organic solvent when the dilution of the salt is as shown in Table 1. The result was confirmed by the experiment on the acetone solution of KI which is described in the following.

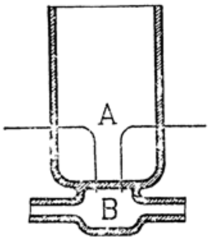

Fig. 2.

A glass vessel which consists of two parts A and B is constructed (Fig. 2). Two platinum wires are sealed in both parts so that the main part of electric capacity lies in A and only a small part in B. The electric capacity is determined in the following three cases; (a) when both A and B are filled with pure acetone, (b) when both A and B are filled with the acetone solution of KI (of a dilution as shown in Table 1.) and (c) when A is filled with pure acetone and B with a solution of such a concentration that the total conductivity is equal to that in the case of (b). The apparent change of capacity caused by the conductivity in the latter two cases should be equal to each other. Therefore the change of the dielectric constant between the solvent and the solution can at once be known if there is any difference of ΔC in these two cases. The result of the experiment shows that no difference can be found within the experimental error which amounts to a few percent, though the value in these two cases is quite different from that in (a). The change of the dielectric constant of acetone can safely be neglected and the correction for the conductivity can be obtained from the difference between ΔC in (a) and that in (b). Table 2 contains the experimental values of ΔC and $\Delta^2 C$ (the difference between ΔC of the solution and that of pure acetone) obtained at the room temperature when the solutions of various conductivities are contained in the vessels I, II, III and IV of X.

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(1) Walden, *Z. physik. Chem.*, **115** (1925), 177; **116** (1925), 261.

TABLE 2.

Conductivity cm^{-1} ohm^{-1}	Vessel I		Vessel II		Vessel III		Vessel IV	
	ΔC	$\Delta^2 C$	ΔC	$\Delta^2 C$	ΔC	$\Delta^2 C$	ΔC	$\Delta^2 C$
48×10^{-5}	3.5	0.9	4.6	1.4	—	—	—	—
26×10^{-5}	3.05	0.45	3.7	0.5	4.55	0.7	5.5	0.9
14×10^{-5}	2.75	0.15	3.4	0.2	4.1	0.25	4.9	0.3
7×10^{-5}	2.65	0.05	3.25	0.05	3.9	0.05	4.7	0.1
3.5×10^{-5}	2.6	0	3.2	0	3.85	0	4.6	0
pure acetone	2.6	—	3.2	—	3.85	—	4.6	—

The aqueous solutions of NaCl etc. give the same result as above, *i.e.* the acetone solution of KI and the aqueous solution of NaCl give the same value of $\Delta^2 C$ when the two have the same conductivity and are contained in the same vessel. Hence $\Delta^2 C$ depends merely upon the conductivity of the medium. Thus $\Delta C'$, the corrected value of the displacement ΔC of the glass plate, from which the dielectric constant is to be calculated, can be simply found from the following equation,

$$\Delta C' = \Delta C - \Delta^2 C$$

$\Delta^2 C$ is to be found graphically for each vessel, combining tables 1 and 2, the value I/I_0 being known from a direct observation.

Experimental Results. The wave length was determined with various combinations of inductance and capacity and the result is shown in Table 3.

TABLE 3.

Inductance cm. (E.M.U.)	Capacity cm. (E.S.U.)	Wave length m.
104	22.0	9.50
115	20.0	9.53
127	17.8	9.45

The wave length is, therefore, 9.5 meters.

The experimental data on the non-absorbents, acetone and ether, and the absorbent glycerine are given in the following tables.

I/I_0 : Ratio of the deflections of galvanometer at resonance,
ΔC : Displacement of glass plate,
$\Delta C'$: Corrected value of ΔC,
ε : Dielectric constant,
K : Electric conductivity which is equivalent to anomalous absorption (cm^{-1} ohm^{-1}).

TABLE 4.
Ethyl ether

Vessel	Temp.	I/I_0	ΔC	ε	ε* (Isnardi)
VII	5	1.0	6.25	4.7	4.6
VI	5	1.0	4.3	4.8	4.6
VII	−24	1.0	7.8	5.6	5.5
VI	−24	1.0	5.2	5.6	5.5
VII	−60	1.0	10.0	6.8	6.6
VI	−60	1.0	6.4	6.6	6.6

TABLE 5.
Acetone

Vessel	Temp.	I/I_0	ΔC	ε	ε† (Graffunder)
I	20	1.0	2.55	21	22.4
II	20	1.0	3.2	22	22.4
I	8	1.0	2.8	23	23.9
II	8	1.0	3.55	24	23.9
III	7	1.0	4.05	24	23.9
IV	7	1.0	4.8	24	23.9
III	− 5	1.0	4.3	25	24.5
IV	− 5	1.0	4.8	24	24.5
I	−13	1.0	3.15	25	25.3
II	−13	1.0	3.9	26	25.3
IV	−15	1.0	5.35	26	25.4
III	−15	1.0	4.65	26	25.4
IV	−47	1.0	6.3	29	
III	−47	1.0	5.45	29	
II	−48	1.0	4.75	30	
I	−48	1.0	3.95	30	
III	−51	1.0	5.25	28	
IV	−51	1.0	6.1	28	
III	−66	1.0	5.8	31	
IV	−67	1.0	6.65	30	

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* These values of ε are obtained by graphical interpolation.
Isnardi, *Phys. Z.*, 22 (1921) 230.

† These values of ε are obtained by graphical interpolation.
Graffunder, *Ann. Physik.* 70 (1923), 225.

TABLE 6.

Glycerine

Vessel	Temp.	ΔC	I/I_0	$\Delta C'$	ε	$K \times 10^5$	ε* (Graffunder)
II	65	5.25	.72	5.25	36	<1	35.2
I	59	4.45	.74	4.45	38	1	36.2
II	50	5.65	.50	5.65	39	2	37.7
I	40	4.9	.48	4.9	41	3	39.4
II	31	6.15	.23	6.15	41	7	40.9
I	25	5.1	.21	5.1	41	10	41.9
II	24	6.4	.14	6.25	42	12	42.0
I	23	5.25	.18	5.2	43	12	42.3
I	22	5.2	.15	5.1	42	15	42.5
I	14	4.95	.09	4.6	37	24	44.0
II	13	5.95	.07	5.5	36	23	44.1
II	12	5.65	.07	5.2	34	23	44.3
I	12	4.55	.09	4.2	34	24	44.3
II	11	5.85	.06	5.3	35	26	44.5
IV	4	6.8	.04	5.9	29	26	46.1
I	3	3.75	.08	3.35	27	26	
I	2	2.75	.08	2.35	19	26	
II	0	3.6	.06	3.05	20	26	
I	−4	1.95	.09	1.6	14	24	
I	−9	1.75	.16	1.65	14	14	
II	−11	1.95	.15	1.8	12	11	
IV	−12	2.4	.12	2.2	11	11	
II	−18	1.05	.26	1.05	8	5	
IV	−21	1.4	.29	1.4	8	4	
IV	−24	1.05	.40	1.05	6	3	
II	−30	0.8	.53	0.8	6	2	
II	−33	0.65	.58	0.65	5	2	
IV	−40	0.8	.72	0.8	5	<1	
IV	−41	0.8	.70	0.8	5	1	
II	−51	0.5	.84	0.5	4	<1	
II	−52	0.35	.86	0.35	3	〃	
IV	−58	0.65	.95	0.65	4	〃	
IV	−61	0.5	.98	0.5	3	〃	

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* Graffunder, loc. cit.

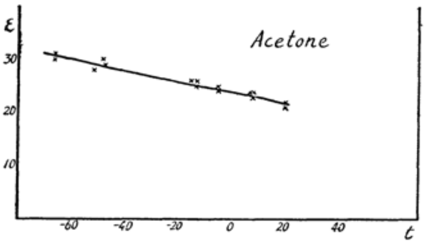

Fig. 3.

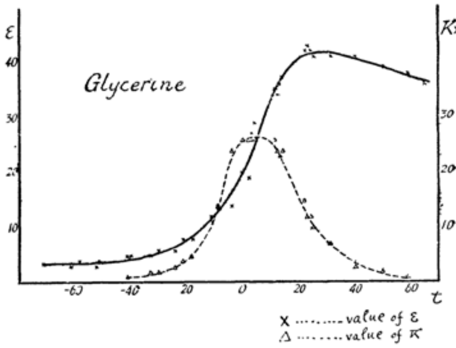

Fig. 4.

Ethyl ether and acetone. (Table 4 and 5, Fig 3). These two substances show no difference between I and I_0 within the limit of the experimental error. The value of ε coincides with that obtained by Isnardi(1) and Graffunder(2) at long wave lengths.

Glycerine. (Table 6, Fig. 4). The anomalous behaviour is quite similar to that at the wave length of 6.1 meters. At low temperatures there is almost no absorption and ε takes a value nearly equal to the square of the refractive indices for the visible light. As the temperature is gradually raised, the absorption of wave takes place, and the value of K increases with ε. K reaches the maximum value at the point where the temperature coefficient of ε is nearly maximum. Then K decreases, but ε still increases till it attains a maximum value. Thence the change of ε is quite normal (i.e. ε decreases as the temperature is raised) and, although there is some absorption in this region, the values of ε obtained are found to coincide with those measured at longer wave lengths.

Further explanation of results will be given in the next paper which will contain the experimental data on monovalent alcohols. The author wishes to express his best thanks to Prof. M. Katayama for his kind guidance.

October, 1925

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(1) Isnardi, loc. cit.

(2) Graffunder, loc. cit.