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

By San-ichiro MIZUSHIMA.

Received February 8, 1926. Published March 28, 1926.

We know that the dielectric constants of many liquid substances have such values that their square roots (i.e. the refractive indices for the long electric waves) are incomparably greater than the indices of refraction for the visible and infra-red rays. These substances are, in general, chemically abnormal liquids. So if the refractive indices (n) for the electromagnetic waves of the wave lengths ranging from the order of those of visible light to

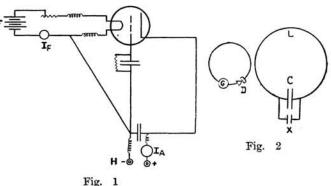
⁽¹⁾ Read before the Chemical Society of Japan, January 17, 1925.

infinity be measured, we may expect that n suffers an enormous change or changes in a certain region of wave length till it attains the large value which is practically independent of wave length. Such a change (i.e. an anomalous dispersion) will be accompanied by an anomalous absorption, if the phenomenon be regarded as analogous to that in the case of the shorter wave lengths.

Although some authors measured the indices⁽¹⁾ of refraction and absorptions⁽²⁾ of short electric waves, the measurements were carried out only at the ordinary temperatures and at the wave length of less than one meter. The following experiments have been undertaken to measure the anomalous dispersion and absorption at various temperatures and for various wave lengths, and to study their relations. In this first report, however, only the description of the experiment by use of the wave of 6.1 meters will be given.

The resonance method is adopted in this experiment. As a oscillation generator, a thermionic bulb is used. Fig. 1 shows the scheme of the generator circuit. H is a high-tension battery of 200 volts, F a filament battery of 6 volts, I_F an ammeter which indicates the filament current and I_A a milliammeter in the anode circuit. H is connected in parallel with the air condenser, the capacity of which is about 1/1000 M.F. A resistance of 10000 ohms shunted by a condenser (also 1/1000 M.F.) is inserted in the grid circuit.

The resonator consists essentially of an inductance L and the two capacities C and X as shown in Fig. 2. C is constructed from two brass bars of rectangular section (9 mm. $\times 5.5$ mm.) placed in parallel position at a distance of 5.5 mm.



Between these two, a plane-parallel glass plate is slided to vary the capacity of C. The liquid to be examined is contained in a small vessel X of about 20 c.c. with platinum wires fused in on opposite sides. The vessel X is con-

Lampa, Wien. Ber., 105 (1896) 587 u. 1049.
 Lang, Wien. Ber., 105 (1896) 253.
 Möbius, Ann. d. Phys., 62 (1920) 293.
 Tear, Phys. Rev., II. 21 (1923) 611.

⁽²⁾ Drude, Z. physik. Chem., 23 (1897) 308. Romanoff, Ann. d. Phys., 69 (1922) 125.

nected in parallel with C. The detector circuit consists of a crystal detector D and a sensitive galvanometer G. All the resonating system is placed so far from the oscillator that the change of the resonating current (or the current at resonance) causes no effect upon the wave length of the oscillator.

At first the second system is adjusted to resonance to the first by sliding the glass plate of C into its suitable position, then the capacity X is filled with the liquid to be examined and the system is again brought into resonance by the same method. If the sample has no absorbing power, the resonating currents will be the same in both cases. This has been shown to be actually the case for normal organic liquids. But if the sample absorbs electric wave, for instance glycerine, the resonating current in the latter case is always considerably less than that in the former.

When the waves of a few meters were used, distilled water, acetone, benzene, the mixtures of acetone and water and those of acetone and benzene show no change of resonating current at ordinary temperatures. This is also the case when the capacity of X is changed to a considerable amount. From these results it is evident that these are non-absorbents of this wave and can be used as standard substances in the measurement of dielectric constants. In order to determine specific constants of each vessel measurements were carried out by use of these non-absorbing substances and the results show that the relation expressed by the equation (1) holds within the limit of experimental error which amounted to a few percent. The effect of reading wires from C to X which have certain small inductance are not perceptible.

 ε is the dielectric constant of the liquid, k the specific proportional constant for the vessel, and ΔC the displacement of the glass plate from the initial position *i.e.* the position when X is filled with air only.

Merck's or Kahlbaum's reagents were used in the experiments. They were dehydrated and then subjected to fractional distillations before use.

Wave Length. If the resonating circuit is placed so far from the detector circuit that the mutual inductance is negligible, the wave length of the oscillation circuit can be calculated from the self-inductance and capacity of the resonator. For this self-inductance a simple circle of copper wire were used in order that the self-inductance L can be calculated from the following formula (L-inductance, R-radious of the circle, ρ -radius of the wire used),

$$L=4\pi R(\ln R/\rho+0.079)\cdots(2)$$

The variable capacity was calibrated, using disc condensers as the standard, the capacities of which were obtained from the following formula:

$$K = \frac{r^2}{4a} + \frac{r}{4\pi} \left(\ln \frac{16\pi r(a+d)}{a^2} + 1 + \frac{d}{a} \ln \frac{a+d}{d} \right) \cdots (3)$$

where K is the capacity, r the radius of the disc, d its thickness, and a the distance between two discs. Table 1 contains the observed values of wave length using various combinations of inductance and capacity. The wave length is 6.1 meters.

TABLE 1.

Inductance cm. (E.M.U.)	Capacity cm. (E.S.U.)	Wave Length m.
413	22.7	6.08
490	19.0	6.06
603	15.45	6.07
622	15.0	6.07

Mean 6.1 Meters

Dielectric Constants and Absorptions. The values of the dielectric constants and the absorptions (expressed by the change of the resonating current) at various temperatures are shown in Table 2. When the substance under examination is an absorbent, X is not a pure capacity but corresponds to a capacity shunted by a considerably low resistance. As the values of ε of such a substance were also calculated from the equivalent pure capacity, the values are only apparent in such a case. Several vessels were used to avoid the constant error characteristic to each vessel. The capacities of Vessels I, II, III are in the ratio 1:1.2:1.5.

TABLE 2.

 ΔC : Displacement of the glass plate. ε : Dielectric constant. I and I_0 : Resonating current when X is filled by the sample and by the air respectively.

Acetone.

Glycerine.

	7	essel I	I.
Temp.	ΔC	ε	I_0
41	3.0	18	1.0
24	3.3	20	1.0
12	3.3	20	1.0
- 3	3.5	21	1.0
-13	3.92	23	1.0
-22	4.1	25	1.0
-36	4.3	26	1.0
-49	4.7	28	1.0
-68	6.0	30	1.0
-69	6.4	32	1.0

	1	Vessel :	I.	V	essel I	II.
Temp.	ΔC	ε	$\frac{I}{I_0}$	ΔC	ε	$\frac{I}{I_0}$
57	4.8	36	.4 .3 .2	8.2	35	.2
46	5.0	37	.3	8.7	37	.2
46 37	5.2	39	.2	9.3	40	.08
30	5.3	40	_	9.6	41	
24	5.4	41	.08	9.7	42	.04
20	5.2	39	.05	9.4	41	.03
18	5.1	38	_	9.2	40	-
15	5.0	38	.04	8.7	37	
6	3.25	25	.05	5.4	24	-
- 8	1.45	12 7	.08	2.2	10	
-23	0.8	7	.5	1.1	6	.2
-23 -45 -70	0.4	4	.9	0.7	4	
-70	0.35	4	1.0	0.6	4	1.0

Methyl alcohol.

Ethyl alcohol.

	Ves	sel I	Vess	el III
Temp.	ε	$\frac{I}{I_0}$	ε	I_0
45	28	.6	27	.4
33	29	.5	29	.4
18	32	.5	33	.2
14	****	-	-	-
10	35	.3	34	.2
0	37	.3	37	.2
- 4	-	-	_	
- 9	39	-	39	.2
-28	44	.2	-	_
-42	49	.1	_	_
-44	70-00	-		-
-54	54	.09	-	1900
-65	55	.08	-	-
-69	57	.04	-	-
-77	58	-	110 0	-
-84	62	.04	-	-
-89	_	_	-	-

63 53 45 34 25 20 10 8 - 4 -13 -18	Ves	sel I	Ves	sel III
Temp.	ε	I_0	ε	I_0
63	18	.9	18	.8
53	19	.8	19	.7
45	21	-	20	_
34	22	.6	22	.5
25	24	-	23	.4
20	24	.6	23	.3
10	26	.5	25	.3
8	27	.4	26	-
- 4	28	.3	27	.2
-13	30	.2	29	.1
-18	30	.2	29	.1
-23	31	.1	-	-
-30	32	.1	31	.04
-32	31	.07	_	
-35		_	32	.05
-46	31	-	30	-
-48	29	.05	29	.03
-58	22	.06	25	.03
-60	-	-	23	.03
-69	19	.05	18	.03
-71	19	.05	-	-

Propyl alcohol.

Isopropyl alcohol.

	Ves	sel I	Vesse	lIII
Temp.	ε	$\frac{I}{I_0}$	ε	I_0
60	15	.9	15	.8
50	16	.9	16	.7
45	17	.8	16	.6
36	18	.7	17	.6
26	19	.6	19	.4
23	20	.5	19	.3
16	22	_	20	.3
15	22	.4	20	_
6	-	- 1	21	.2
3	23	.2	21	.1
- 8	23	2	22	.1
-20	21	.1	21 ·	.05
-31	17	.05	17	.03
-41	13	.07	11	.05
-51	8	.1	8	.06
-59	6	.2	6	.1
-69	5	.2	5	.1

	Ves	sel I	Vessel I Vessel I		
Temp.	ε	I_0	8	$\frac{I}{I_0}$	
55	15	.9 .9 .8 .7 .6 .5 .5 .3 .3 .1 .1	14	.8 .7	
45	16	.9	15	.7	
37	16	.8	16		
29	17	.7		_	
26	19	.6	18	.4	
20	19	.5			
16	20	.5	20	.3	
9	21	.3	-		
9	21	.3	18 20 21 21 22 22 22 17 —	- - - - - - - - - - - - - - - - - - -	
	21	.1		_	
- 4 - 8	23	.1	22	.05	
-16	22	.08	22	.05 .03 	
-19	19	.04	-	_	
-29	16	.08	17	2	
-31	13	.09	V	_	
-39	10	.1	_		
-42	8	.1	9	.05	
-47	7	.2	-		
-54	5	.2	6	.1	
-42 -47 -54 -56	8 7 5 6 4	.1 .1 .2 .2 .2 .2 .4	_	-	
-69	4	.4	5	.2	

Butyl alcohol.

Isobutyl alcohol.

		I WIOOII	979								
	Ves	Vessel I		sel III		Ves	sel I	Vessel III			
Temp.	ϵ $\overline{I_0}$ ϵ $\overline{I_0}$	Temp.	ε	$-\frac{I}{I_0}$	ε	I_0					
59	13	.8	=	_	57	13	.8	12	.8		
58	-	- 1	13	.7	45	14	.8	13	.6		
48	14	.6	14	.5	38	15	.7	15	.6		
37	16	.5	15	1.	30	16	.5	15	.3		
27	17	.4	16	.2	22	16	.4	16	.2		
18	17	.2	18	.1			1	17			
16	18	-	18	.1	18	17	.3		.1		
13	18	_	18		16	18	.2	17	.1		
8 7	19	-	19	_	10	18	.2	18	.09		
7	19	-	19	.07	1	18	.2	17	.09		
4	19			-	-10	13	.1	13	.0-		
- 4	18	.06	18	.03	-19	9	.09	9	.07		
- 9	18	-	18	_	-28	6	1200	6	.08		
-15	17	.09	18	.03	-42	5	_	5	.2		
-22	2 500	-	12	-	-5 3	4	.5	4	.2		
-29	10	.1	11	.05		4		3			
-37	7	1 -	7	-	-58	4	.6	1.000	.4		
-47	6	.2	5	.1	-62	-	_	3	.6		
-67	4	.4	4	.2	-63	4	.7	_	-		

Amyl alcohol.

	Vess	el I	Vess	el II	Vess	el III		Ves	sel I	Vess	el II	Vess	el III
Temp.	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$	Temp.	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
63	10.4	_	_	_	10	.7	14	15	.2	_	-	15	.1
56	-	_	11	.8	-	_	9	_	200	14	.09	_	_
5 6 50	12	-	_	_	11	-	4	13	.1		_	14	.08
45		-	12	.6	-	-	- 4	_	-	12	.06	_	-
45 39	13	.7	_	- '	12	.5	-10	9	.1	-	5-1	9	.06
35	-	_	13	.5	-	-	-11	-	-	9	.06	_	7777
31	14	.4	-	_	14	.3	-20	7	.2	7	-	6	.08
29	_		13	.4	-	-	-33	4	.3	5	.3	4	.2
24	15	.4	-		14	.2	-41	4	.5	3	.4	4	.3
20	-	_	14	.3	_	_	-48	4	.5	3	.5	4	.4
16	15	.2	14	.2	14	.2	-55	— .	_	3	.6	_	_

Acetone. The resonating currents show no change at all temperatures. The value of ε increases as the temperature is lowered. Nothing anomalous can be found.

Glycerine. The behavior is quite different from that of acetone. Though ε changes at higher temperatures quite similarly to that of an ordinary substance, it attains a maximum value near ordinary temperature, then it decreases till it attains a value almost equal to the square of the refractive indices for visible light. As to the resonating current it decreases as the temperature is lowered, then it passes through a minimum and at last I/I_0 becomes unity. The small value of ε at the low temperature is no more an apparent one, because there is no absorption at all. Thus in this case the change of dielectric constants is quite different from that of an ordinary substance, though we are not still aware of its true value for the case in which the absorption takes place. It is evident that we are dealing here with an anomalous dispersion accompanied by an anomalous absorption as was expected.

Alcohols. Of alcohols—ethyl, propyl, isopropyl, butyl, isobutyl and amyl, the results are, in general, similar to that of glycerine. Methyl alcohol gives no maximum of apparent dielectric constants, but as there exists a considerable anomalous absorption at lower temperatures it can be expected that at still lower temperatures it will also show an anomalous change of ε .

As given above, these alcohols, monovalent as well as polyvalent, show anomalous absorptions accompanied by anomalous dispersions of the electromagnetic oscillation of the wave length of 6.1 meters. It seems that the cause of this absorption lies in the hydroxyl group contained in these compounds⁽¹⁾. This fact, therefore, may be used as one of the criterions to ascertain whether a compound contains this group or not. From the point of view of the classical electro-magnetic theory these substances must have their characteristic oscillations, the wave length of which corresponds to that used in this experiment. Then it should be admitted that the wave length of these characteristic oscillations varies with the temperature.

In conclusion I desire to express my best thanks to Prof. M. Katayama for his kind guidance and to Assistant Prof. D. Nukiyama for his advice on electricity.

October, 1924.

Laboratory of Physical Chemistry, Faculty of Science, Tokyo Imperial University.

⁽¹⁾ Drude, loc. cit.