# ON THE ANOMALOUS DISPERSION AND ABSORPTION OF ELECTRIC WAVES. PART V. ANOMALOUS DISPERSION AND DEBYE'S DIPOLE THEORY (CONTINUED).(1)

By San-ichiro MIZUSHIMA.

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Electric waves of the wave lengths of 3.08 metres and 50 metres were generated. Measurements of dielectric constants and absorptions were carried out according to the method described in Part II of the present report(2). The experimental results were interpolated and the values at every ten degrees of temperature are shown in the following tables.

$\varepsilon_{obs.}$ : Dielectric constant,
$\varepsilon_0$ : Static dielectric constant,
$\varepsilon_\infty$ : Square of the index of refraction for visible light (D line),
K : Electric conductivity which is equivalent to anomalous absorption ($cm.^{-1}$ $ohm^{-1}$),
$\eta$ : Viscosity.

TABLE 1.

Ethyl alcohol

$a = 1.8 \times 10^{-8}$ cm.

| Temp. | $\eta$ | $\varepsilon_0$ | $\lambda=50$ m. | | | $\lambda=3.08$ m. | | | $\varepsilon_\infty$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | $\varepsilon_{calc.}$ | $\varepsilon_{obs.}$ | $K \times 10^5$ | $\varepsilon_{calc.}$ | $\varepsilon_{obs.}$ | $K \times 10^5$ | |
| 60° | — | — | — | — | — | — | 20 | 3 | — |
| 50 | — | — | — | — | — | — | 21 | 4 | — |
| 40 | — | — | — | — | — | — | 22.5 | 5 | — |
| 30 | — | — | — | 23.5 | < 1.0 | — | 23.5 | 8 | — |
| 20 | 0.0119 | 25.8 | 26 | 25 | 〃 | 25 | 25 | 13 | 1.85 |
| 10 | 0.0145 | 27.0 | 27 | 26.5 | 〃 | 26 | 26.5 | 21 | 1.86 |
| 0 | 0.0177 | 28.4 | 28 | 28 | 〃 | 26.5 | 28 | 32 | 1.88 |
| −10 | 0.0218 | 30.3 | 30 | 29.5 | 〃 | 26.5 | 28 | 49 | 1.90 |
| −20 | 0.0276 | 32.0 | 32 | 31.5 | 〃 | 25.5 | 26 | 72 | 1.91 |
| −30 | 0.0358 | 33.7 | 34 | 33 | 〃 | 23 | 21.5 | 80 | 1.92 |
| −40 | 0.0490 | 35.3 | 35 | 35 | 〃 | 18 | 17.5 | 80 | 1.94 |
| −50 | 0.0684 | 37.6 | 37 | 37 | 〃 | 13 | 13.5 | 67 | 1.96 |
| −60 | 0.0959 | 39.7 | 39 | 39 | 1.2 | 9 | 9 | 47 | 1.98 |

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(1) Details of these papers will appear in near future in the *Journal of the Faculty of Science, Imperial University of Tokyo.*

(2) Mizushima, this journal, 1 (1926), 83.

## TABLE 2.

Propyl alcohol

$a=2.0\times10^{-8}$ cm.

| Temp. | $\eta$ | $\varepsilon_0$ | $\lambda=50$ m. | | | $\lambda=3.08$ m. | | | $\varepsilon_\infty$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | $\varepsilon_{\text{calc.}}$ | $\varepsilon_{\text{obs.}}$ | $K\times10^5$ | $\varepsilon_{\text{calc.}}$ | $\varepsilon_{\text{obs.}}$ | $K\times10^5$ | |
| 60° | — | — | — | — | — | — | 17 | 3 | — |
| 50 | — | — | — | 17 | < 1.0 | — | 18 | 5 | — |
| 40 | — | — | — | 18.5 | 〃 | — | 19 | 8 | — |
| 30 | — | — | — | 20 | 〃 | — | 20 | 12 | — |
| 20 | 0.0226 | 22.2 | 22 | 21.5 | 〃 | 20 | 20.5 | 21 | 1.92 |
| 10 | 0.0292 | 23.5 | 23 | 23 | 〃 | 19 | 20 | 34 | 1.94 |
| 0 | 0.0388 | 24.8 | 25 | 24 | 〃 | 17 | 17.5 | 48 | 1.95 |
| −10 | 0.0513 | 26.2 | 26 | 25.5 | 〃 | 14 | 14 | 58 | 1.97 |
| −20 | 0.0716 | 27.5 | 27.5 | 27.5 | 〃 | 10.5 | 11 | 50 | 1.98 |
| −30 | 0.103 | 29.0 | 28.5 | 29 | 〃 | 7 | 8 | 34 | 2.00 |
| −40 | 0.154 | 30.5 | 29 | 30 | 1.2 | 5 | 6.5 | 22 | 2.02 |
| −50 | 0.236 | 32.0 | 27.5 | 29 | 2.7 | 3.5 | 5.5 | 14 | 2.03 |
| −60 | 0.386 | 33.7 | 22.5 | 24 | 4.8 | 3 | 5 | 9 | 2.05 |

## TABLE 3.

Isobutyl alcohol

$a=2.0\times10^{-8}$ cm.

| Temp. | $\eta$ | $\varepsilon_0$ | $\lambda=50$ m. | | | $\lambda=3.08$ m. | | | $\varepsilon_\infty$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | $\varepsilon_{\text{calc.}}$ | $\varepsilon_{\text{obs.}}$ | $K\times10^5$ | $\varepsilon_{\text{calc.}}$ | $\varepsilon_{\text{obs.}}$ | $K\times10^5$ | |
| 60° | — | — | — | — | — | — | 14 | 3 | — |
| 50 | — | — | — | 16 | < 1.0 | — | 15 | 6 | — |
| 40 | — | — | — | 17 | 〃 | — | 16 | 10 | — |
| 30 | — | — | — | 18.5 | 〃 | — | 16.5 | 18 | — |
| 20 | 0.0391 | 20.0 | 20 | 19.5 | 〃 | 15.5 | 16 | 29 | 1.95 |
| 10 | 0.0555 | 21.0 | 21 | 21 | 〃 | 13 | 13 | 39 | 1.97 |
| 0 | 0.0804 | 21.8 | 22 | 22 | 〃 | 10 | 10 | 42 | 1.99 |
| −10 | 0.116 | 23.2 | 23 | 23.5 | 〃 | 7 | 6.5 | 35 | 2.00 |
| −20 | 0.182 | 24.5 | 23.5 | 24 | 1.3 | 4.5 | 4.5 | 17 | 2.02 |
| −30 | 0.30 | 25.7 | 22.5 | 23.5 | 2.6 | 3 | 4 | 7 | 2.03 |
| −40 | 0.56 | 27.0 | 17.5 | 18.5 | 4.1 | 2.5 | 3.5 | 4 | 2.05 |
| −50 | 1.14 | 29.0 | 10 | 10 | 4.0 | 2 | 3 | 3 | 2.07 |
| −60 | — | — | — | 6 | 2.6 | — | 3 | 2 | — |

### TABLE 4.

Amyl alcohol

$a=2.1\times10^{-8}$ cm.

| Temp. | $\eta$ | $\varepsilon_0$ | $\lambda=50$ m. | | | $\lambda=3.08$ m. | | | $\varepsilon_\infty$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | $\varepsilon_{\text{calc.}}$ | $\varepsilon_{\text{obs.}}$ | $K\times10^5$ | $\varepsilon_{\text{calc.}}$ | $\varepsilon_{\text{obs.}}$ | $K\times10^5$ | |
| 60° | — | — | — | — | — | — | 12 | 3 | — |
| 50 | — | — | — | — | — | — | 13 | 5 | — |
| 40 | — | — | — | — | — | — | 13.5 | 9 | — |
| 30 | — | — | — | — | — | — | 13.5 | 17 | — |
| 20 | 0.0437 | 16.0 | 16 | 15 | $<1.0$ | 13 | 13 | 26 | 1.98 |
| 10 | 0.061 | 16.8 | 17 | 16.5 | 〃 | 10.5 | 10.5 | 33 | 2.00 |
| 0 | 0.0876 | 17.5 | 17.5 | 17.5 | 〃 | 7.5 | 7.5 | 30 | 2.02 |
| −10 | 0.130 | 18.6 | 18.5 | 18.5 | 〃 | 5.5 | 5.5 | 20 | 2.03 |
| −20 | 0.207 | 19.7 | 18.5 | 19 | 1.0 | 4 | 4 | 10 | 2.05 |
| −30 | 0.33 | 20.8 | 18 | 17.5 | 2.2 | 3 | 3.5 | 4 | 2.07 |
| −40 | 0.58 | 21.8 | 14 | 13 | 3.6 | 2.5 | 3 | 3 | 2.08 |
| −50 | 1.01 | 23.0 | 9 | 8 | 3.0 | 2 | 3 | 2 | 2.10 |
| −60 | — | — | — | 5.5 | 1.7 | — | 3 | 2 | — |

### TABLE 5.

Glycerine

| Temp. | $\varepsilon$ $\lambda=1000$ m. (Graffunder) | $\lambda=50$ m. | | $\lambda=3.08$ m. | | $\varepsilon$ $\lambda=1.36$ m. (Bock) |
|---|---|---|---|---|---|---|
| | | $\varepsilon_{\text{obs.}}$ | $K\times10^5$ | $\varepsilon_{\text{obs.}}$ | $K\times10^5$ | |
| 60° | 36 | — | — | — | — | 35 |
| 50 | 38 | 37 | $<1.0$ | 40 | 36 | 36 |
| 40 | 39 | 39 | 〃 | 40.5 | 58 | 33 |
| 30 | 41 | 40.5 | 〃 | 38 | 90 | 25 |
| 20 | 43 | 43 | 〃 | 28.5 | 95 | 14 |
| 10 | 45 | 44 | 2.0 | 14 | 55 | 5 |
| 0 | 47 | 36 | 4.0 | 9 | 30 | 3.5 |
| −10 | — | 23 | 5.6 | 7 | 14 | 3 |
| −20 | — | 13 | 2.4 | 5 | 6 | 3 |
| −30 | — | 8 | $<1.0$ | 4.5 | 3 | 3 |
| −40 | — | 6 | 〃 | 4 | $<2$ | 3 |
| −50 | — | 5 | 〃 | 3.5 | 〃 | 3 |
| −60 | — | 4.5 | 〃 | 3 | 〃 | 3 |

The variation of dielectric constants and absorptions due to temperature observed at a constant wave length is, in general, quite analogous to that for the wave of 9.5 metres (see Part II and III).(1)

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(1) Mizushima, this journal, **1** (1926), 83 & 115.

The values of $\varepsilon$ at higher temperatures are independent of wave length and equal to those for static field even for the wave length of 3.08 metres. As the temperature is gradually lowered, the absorption of wave becomes stronger and $\varepsilon$ undergoes a great change at a certain wave length. For instance at $-20°$, $\varepsilon$ of amyl alcohol for the wave length of 50 metres is 19, a value not far from the static dielectric constant, then $\varepsilon$ decreases to 4, a value approaching to the square of the refractive index for the visible light ($N_v^2$). At still lower temperatures e.g. at $-60'$ where the absorption of wave again decreases, all the values of $\varepsilon$ for different wave lengths approach to one another and are not far from $N_v^2$. This was not observed for ethyl alcohol, but if the experiment could be carried out at sufficiently low temperatures, liquid ethyl alcohol would also show this end of anomalous dispersion.

In short the dielectric constants of alcohols and glycerine change continuously from the large value for the static field to the small value nearly equal to $N_v^2$ and the region of anomalous dispersion accompanying intense absorption shifts to longer wave lengths as the temperature is lowered.

Here we have a relation between the anomalous dispersion and absorption of electromagnetic waves, which is quite analogous to that for the visible light. But it should be noticed that an absorption band in the visible as well as in the infra-red or ultra-violet parts is not so much effected by the temperature variation, while a band in the electric spectrum undergoes an enormous effect and the band shifts to the longer wave lengths as the temperature is lowered. From the measurement of the anomalous electric absorption by Drude,(1) the wave length of 70 cm. is often adopted, without the indication of temperature, as the characteristic wave length of alcohols, but when the absorption band in the electric spectrum is considered, the indication of temperature must not be forgotten as is shown above.(2)

As to the anomalous absorption for a definite wave length, Drude noticed in his paper that the absorption by alcohols becomes stronger as the temperature is lowered. However, such is the case only at comparatively higher temperatures. As the temperature is lowered, the absorption reaches a maximum, then decreases till it almost disappears. It is evident that all of the Drude's experiments were carried out at the temperatures higher than that for this maximum absorption.

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Now the above results can be discussed from the view-point of Debye's dipole theory, of which a short explanation was already given in Part IV.(3)

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(1) Drude, *Z. physik. Chem.*, **23** (1897), 267.
(2) Landolt-Börnstein's "Tabellen," (1923), p. 807.
(3) Mizushima, this journal **1** (1926), 143.
Debye, *Verh. Deut. Physik. Ges.* **15** (1913), 770.

The distribution function of dipole axes for the angle $\theta$ under the periodic force $Ke^{i\omega t}$ is

$$F=A\left(1+\frac{1}{1+\frac{i\omega\rho}{kT}}\ \frac{m}{kT}\ Ke^{i\omega t}\cos\theta\right)\cdots\cdots\cdots\cdots\cdots\cdots(1)$$

where

$$\rho=8\pi\eta a^3$$

and $A$ is a constant, $\eta$ the viscosity, $a$ the radius of the molecule, $m$ the moment of dipole, $k$ Boltzmann's constant and $T$ the absolute temperature.

This becomes for a static field :

$$F_0=A\left(1+\frac{m}{kT}\ K\cos\theta\right)\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$

The difference in the distribution between a static and an alternating field is, therefore, determined by the expression $\left(1+\frac{i\omega\rho}{kT}\right)$, in which

$$\frac{\rho}{kT}=\frac{8\pi\eta a^3}{kT}=\tau\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(3)$$

expresses the time of relaxation of the molecule. So long as the period of external fleld is very great as compared with $\tau$, the distribution of the dipole axes will remain practically constant. Consequently the dielectric polarization is independent of wave length and equal to that for the static field. If, however, the external period approaches to the time of relaxation, $F$ becomes different from $F_0$ and the medium will show anomalous dispersion. We see in equation (3) that the value of $\tau$ is proportional to the viscosity $\eta$ and the cube of the molecular radius $a^3$ and inversely proportional to the absolute temperature $T$. Therefore the anomalous region will shift to the longer wave lengths as the temperature is lowered and the viscosity becomes greater. The effect will be the same as we proceed from lower to higher alcohols, because the molecular radius as well as the viscosity becomes greater. These are all what are confirmed by the above experiments.

From equation (1) we can calculate the dielectric constant $\varepsilon$ for an alternating field of the frequency $\frac{\omega}{2\pi}$,

$$\varepsilon=\left\{\frac{\left(\frac{\varepsilon_0}{\varepsilon_0+2}\right)^2+\frac{\omega^2\rho^2}{k^2T^2}\left(\frac{\varepsilon_\infty}{\varepsilon_\infty+2}\right)^2}{\left(\frac{1}{\varepsilon_0+2}\right)^2+\frac{\omega^2\rho^2}{k^2T^2}\left(\frac{1}{\varepsilon_\infty+2}\right)^2}\right\}^{\frac{1}{2}}\cos^2\frac{\varphi}{2}$$

where

$$\tan\varphi=\frac{\omega\rho}{kT}\,\frac{\varepsilon_0+2}{\varepsilon_\infty+2}\,\frac{1-\dfrac{\varepsilon_\infty}{\varepsilon_0}}{1+\dfrac{\omega^2\rho^2}{k^2T^2}\left(\dfrac{\varepsilon_0+2}{\varepsilon_\infty+2}\right)^2\dfrac{\varepsilon_\infty}{\varepsilon_0}}$$

The values of $\varepsilon_{\text{calc.}}$ are calculated for the wave length of 3.08 metres and 50 metres according to the method as explained in Part IV(1) and are compared with the observed values ($\varepsilon_{\text{obs.}}$). As shown in the above tables, $\varepsilon_{\text{calc.}}$ agrees pretty well with $\varepsilon_{\text{obs.}}$

For glycerine we have no data for $a$. Therefore no systematic discussion can be made. If, however, we take at 18° the value of $\varepsilon_0$ equal to 43 (Graffunder(2)), that of $\eta$ to 10.69 (Jones(3)), that of $\varepsilon_\infty$ to 2 and that of $\varepsilon_{\text{obs.}}$ to 25.5 (present experiment), then we obtain the following value of $a$ for glycerine :

$$a=2.8\times10^{-9}\text{ cm.}$$

This is not a reasonable value, because the molecular radius is of the order of $10^{-8}$ cm. even for simple diatomic molecules and that for a complex molecule such as glycerine must be greater than this. We must, therefore, agree with Bock(4) that Debye's formula does not hold for glycerine. As the viscosity of glycerine is abnormally great, it is very doubtful whether $\eta$ in the resistance term $8\pi\eta a^3$ is equivalent to the mass viscosity of glycerine. If glycerine be a colloidal system and its mass viscosity must be considered as the viscosity of heterogeneous mixture,(5) the effective viscosity acting on the rotation of a molecule will be quite different from ordinary viscosity. Then we can naturally consider the glycerine to be an exception for Debye's theory.

Allowing this exception, the result of the author's experiment may be considered to be the first experimental evidence of the dipole theory on the anomalous dispersion of electric waves.

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Chemical Institute, Faculty of Science,
Tokyo Imperial University.

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(1) Loc. cit.

(2) Graffunder, *Ann. Physik.* **70** (1923), 225.

(3) Jones, *Phil Mag.*, (5) **37** (1894), 451.

(4) Bock, *Z. Physik*, **31** (1925), 534.

(5) Einstein, *Ann. Physik*, **19** (1906), 289.