Determination of Dielectric Constant and Loss Factor by Free Wave Method. III. Measurement on Aliphatic Alcohols at the Wavelength of 1.38 cm.

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The theory of determining the dielectric constant and the loss factor of liquids by the free wave method has been developed by M. Yasumi.[1] The dielectric properties of various liquids have been investigated in the microwave region (wavelength=9.8, 4.5 and 3.24 cm.) in our laboratory[2,3,4], and several interesting results have been obtained.

Debye was the first who succeeded to explain theoretically the anomalous dispersion and the absorption of electric wave by polar substances[5]. The basic idea for the assumption of the internal field seems not to be entirely satisfactory. Nevertheless the assumption of the single relaxation time seems to be valid from the experimental point of view[4,6-10]. The validity of this assumption is being kept under consideration in our laboratory and is justified when we adopt a suitable internal field[11,12]. Assuming the single relaxation time, the following equations are shown to be valid irrespective of the relaxation mechanism.

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1+x^2}, \tag{1}$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)}{1+x^2} x, \tag{2}$$

$$x = \omega\tau, \tag{3}$$

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1) M. Yasumi, This Bulletin, **24**, 53 (1951).

2) M. Yasumi, K. Nukazawa and S. Mizushima, This Bulletin, **24**, 60 (1951).

3) M. Yasumi, H. Okabayashi, M. Shirai and S. Mizushima, *J. Chem. Phys.*, **19**, 978 (1951).

4) M. Yasumi, M. Shirai and S. Mizushima, This Bulletin, **25**, 133 (1952).

5) P. Debye, "Polare Molekeln", Leipzig: Hirzel (1929).

6) A. Schallachmach, *Trans. Faraday Soc.*, **42A**, 180 (1946).

7) C. H. Collie, J. B. Hasted and D. M. Ritson, *Proc. Phys. Soc.*, (London), **60**, 145 (1948).

8) J. B. Hasted, G. H. Haggis and P. Hutton, *Trans. Faraday Soc.*, **47**, 577 (1951).

9) G. H. Haggis, J. B. Hasted and T. J. Buchanan, *J. Chem. Phys.*, **20**, 1452 (1952).

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12) M. Yasumi and H. Komooka (to be published).

where ε' is the dielectric constant, ε'' the loss factor and ω the angular frequency. ε_0 and ε_∞ are the values of the dielectric constant at $x=0$ and $x=\infty$ respectively. τ is called the relaxation time and is related to the characteristic frequency λ_s as follows.

$$\lambda_s=2\pi c\tau, \tag{4}$$

where c denotes the velocity of light.

Much of our interest is concerned with the values of ε_∞ for the liquids. In the earlier works,[13] the value of ε_∞ was assumed to be identical with the value of the square of the refractive index $(n_{opt})^2$ at optical regions. If the liquids show marked absorption spectra in infra-red region, the $(n_{opt})^2$ is not identical with ε_∞. The origin of the difference is due partly to the infra-red-active interatomic vibrations in a molecule and partly to the intermolecular vibrations in the liquid structure.

In our preliminary work[4], the dielectric constant and the loss factor were measured at the wavelength of 3.24 cm., and the values of ε_∞ were calculated, assuming the validity of Eqs. (1) and (2). It was concluded there that the atomic polarizations due to the liquid structure are almost constant for various aliphatic alcohols investigated. The obtained result was concerned, however, only with the data at the wavelength of 3.24 cm. The result must be confirmed for the other frequencies.

In the present work, the dielectric constant and the loss factor were measured at the wavelength of 1.38 cm. The method of determining the dielectric constant and the loss factor of the liquids was described by M. Yasumi.[1] The important points will be repeated here. The linearly polarized plane wave of the wavelength λ is emitted vertically into the free space. When the wave comes to the mercury surface, the perfect standing-wave pattern may appear in the space above the mercury surface. If the liquid layer is placed on mercury, the amplitudes of the incident and reflected waves will be generally different. Also the crystal detector shows the imperfect standing-wave when the position of the detector is shifted vertically from the liquid surface to the free space. If the crystal detector obeys the square law, the ratio of the maximum-to the minimum-current induced in the detector, I_M/I_m, is expressed by the following equation,

$$I_M/I_m=(1+R)^2/(1-R)^2. \tag{5}$$

where R^2 is the reflection coefficient of the system consisting of the liquid layer of the thickness d and the mercury layer. Such measurements are made at different thicknesses of the liquid layer.

The reflection coefficient R^2 is expressed as follows:

$$R^2=\frac{\sin h^2\left(\frac{2\pi kd}{\lambda}+\frac{1}{2}\ln R_{12}\right)+\cos^2\left(\frac{2\pi nd}{\lambda}-\frac{\gamma}{2}\right)}{\sin h^2\left(\frac{2\pi kd}{\lambda}-\frac{1}{2}\ln R_{12}\right)+\cos^2\left(\frac{2\pi nd}{\lambda}+\frac{\gamma}{2}\right)}, \tag{6}$$

where n and k are the refractive index and the absorption coefficient of liquid respectively, and further R_{12} and γ are expressed as

$$R_{12}{}^2=\frac{(n-1)^2+k^2}{(n+1)^2+k^2},\quad \tan\gamma=\frac{2k}{n^2-1+k^2}. \tag{7}$$

The real part ε' and the imaginary part ε'' of the complex dielectric constant are related to n and k in the following manner,

$$\varepsilon'=n^2-k^2,\quad \varepsilon''=2nk. \tag{8}$$

It is more convenient to choose as parameters in Eq. (2) n and k than ε' and ε'', as easily seen from Eqs. (6) and (7).

Given n and k, we can use Eqs. (6) and (7) to calculate the reflection coefficient R^2 for the various thickness d and draw the curve of R *versus* d. Here, it is convenient to take d/λ as the abscissa instead of d because in Eq. (6) the thickness d appears always in the form of d/λ.

The method of obtaining the value of n and k for the liquid concerned is as follows. First we obtain the values of I_M/I_m for various thicknesses experimentally. Secondly we calculate the value of R for each value of d/λ. Then we draw the curve of R *versus* d/λ. This experimentally obtained curve is compared with those calculated by Eqs. (6) and (7) for various n and k. The values of n and k assumed in the theoretical curve which fit most satisfactorily the experimental curve, will be taken as values for the liquid investigated. In practice, the interpolation method is used. To confirm whether the values of n and k thus determined are the fittest or not, we make the curve R *versus* d/λ for the values of n and k thus obtained, and compare it with the experimental curve.

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13) S. Mizushima, *Sci. Papers Inst. Phys. Chem. Res.*, (Tokyo), 9, 109 (1928).

Apparatus

The apparatus constructed is shown as a block diagram in Fig. 1.

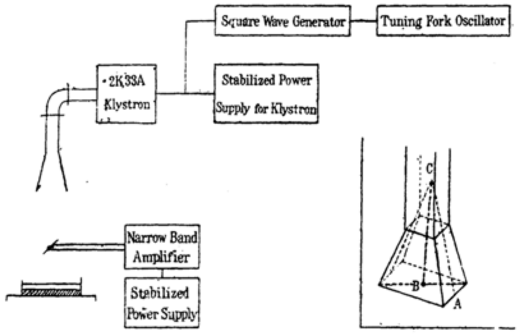

Fig. 1. The block diagram of our apparatus.

A type 2K33A reflex klystron is used as a source of the radiation. The high voltage power supply for the klystron must be highly stabilized by an electronic device because the output power and the frequency of the reflex klystron are extremely sensitive to the beam voltage and the reflector voltage. Our circuit diagram of the voltage stabilizer is shown in Fig. 2.

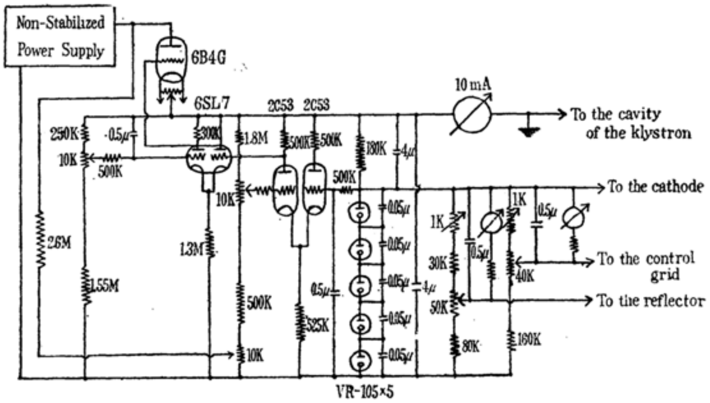

Fig. 2. The high voltage stabilizer for the klystron.

Modulation of the microwave source makes it possible to use a. c. amplification of the signal from the crystal detector and to shorten the time required for each measurement more than to use a galvanometer. For the standing-wave measurement, the percentage of the amplitude modulation should be large, but the frequency modulation must be avoided. Therefore, the "on-off" modulation, with a square modulation envelope, is preferred. Modulation is introduced in the reflector circuit by a square-wave voltage superposed on the steady-state reflector voltage. The square-wave generator is synchronized with the tuning fork oscillator of 1000 c/s., and is constructed so that on- and off-states have almost equal durations, and the rise- and fall-times are extremely short[14].

The electromagnetic horn is connected with the cavity of the klystron through an E-bend waveguide. In order that the wavefront at the aperture may approximate a plane, the difference between the distances from the point C to the center B and to the point A on the edge of the aperture (refer to Fig. 1) is designed to be smaller than $\lambda/8$. The dimension of the aperture is $7.5\times7.5\,\mathrm{cm}^2$. The waveguide connected with the cavity of the klystron has a section of $1.07\times0.43\,\mathrm{cm}^2$ and is operated in a mode H_{01} when the wavelength is 1.38 cm. The electric field in the waveguide makes a right angle to its larger side. Therefore if the waveguide is enlarged gradually to the aperture of the horn, the electric field in the free space is kept in a fixed direction. Thus the radiated wave from the horn is linearly polarized.

The distance between the aperture of the horn and the surface of mercury is about 75 cm., so that the obtained radiation behaves like the plane wave near the liquid surface.

The vessel is made of wood and lacquered, and its dimension is $20\times20\,\mathrm{cm}^2$. This area is sufficiently large to remove the effect of the edges The thickness of the liquid layer is determined from the volume of the liquid poured in.

The crystal detector is made of a tungsten wire and a small pellet of silicon crystal picked out from a commercial crystal detector, 1N23B. Two leads of phosphor bronze which support the crystal and the wire are bound by a rubber ring to adjust the pressure of the tungsten wire against the silicon crystal. The crystal detector so constructed is stably fixed except in the case of a great mechanical shock. The detector system is arranged so that the direction from the tungsten wire to the crystal is parallel to the electric field of the linearly polarized wave. This

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[14] C. G. Montgomery, "Technique of Microwave Measurements", McGraw-Hill Book Company, Inc., New York and London (1947).

detector is shifted vertically to the liquid surface by the micrometer.

The signal of the square-wave from the crystal detector is amplified and introduced in an indicating ammeter of 1 m amp. Because some frequency modulation may occur during the rise- and fall-times of the modulating square-wave, the tuning amplifier is used in order to prevent a spurious signal. The frequency sensitivity of the amplifier is provided by a twin-T feedback network tuned in the 1000 c/s[14].

On adjusting the whole apparatus, the important points to be kept in mind are to determine the region in which the electric field may be measured by the crystal detector, and to construct a sufficiently small crystal detector, so that it might not disturb the radiation field except so slightly as to be negligible, and further to adjust the contact between the wire and the pellet of silicon crystal in order to give a high sensitivity to the microwave field.

Near the aperture of the horn, the radiation pattern is complicated, and far from the plane wave. Also because we cannot place a liquid layer in the infinite and empty space, we must choose the region near the liquid surface in order to avoid the effects of other bodies, for example, of the walls and of the supporter of the vessel, etc. On the other hand, the disturbance of the detector may be detected as a departure from the (sine)^2 law for the standing-wave pattern which appears on the mercury layer.

By trial and error, we adjusted the whole system in order that it may be operated under the best conditions, changing the frequency of the radiation source slightly. As the result we knew that the detector may be shifted in the region near the height 6 cm. from the liquid layer. The dimension of the crystal detector which was used is shown in Fig. 3. The resulting standing-wave pattern on the mercury layer showed that near the above-mentioned height the maximum values of the induced current fluctuated within ±1 percent, and that the minimum values were recognized as zero as far as we used the ammeter of 1 m amp. as an indicating meter. The maximum point shifted about 0.15 mm from the middle point of two successive minimum points towards the radiation source. The induced currents showed the square law except in the region where the current was very small. We can determine the wavelength within the accuracy of ±0.2 percent from this perfect standing-wave pattern. In many cases the wavelength was 1.378 cm.

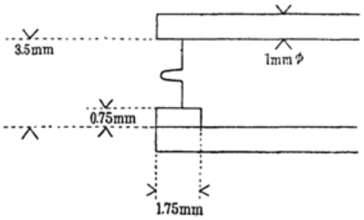

Fig. 3. The dimension of the crystal detector.

Materials

Methyl alcohol: Commercial methyl alcohol is boiled with freshly burnt lime under reflux and distilled. Then the distillate is refluxed with silver nitrate and distilled. The distillate is dried over magnesium activated with iodine, b. p. 67.0–67.4°C.

Ethyl alcohol is purified by the same procedure as methyl alcohol, b. p. 77.8–78.3°C.

Purified *n*-butyl alcohol is obtained by means of the efficient fractionating column constructed by T. Tamura[15], b. p. 117.0–117.2°C.

Isobutyl alcohol is treated with freshly burnt lime, and then the distillate is dried over anhydrous copper sulphate, b. p. 107.5–108.2°C.

Tertiary butyl alcohol is dried over sodium hydroxide and then fractionated by means of the above-mentioned column, b. p. 83.5–83.8°C.

Measurements

Each measurement is operated half an hour later, after the whole apparatus was switched on. At first we measure the standing-wave pattern when the vessel contains only mercury. The wavelength is determined from it. Thereafter a certain amount of liquid is poured in, and we measure the standing-wave ratio by shifting the crystal detector vertically to the liquid surface. These operations are repeated. Finally we can draw the curve R *versus* d/λ using the table of the standing-wave ratio *versus* the square root of the reflection coefficient, R.

For $n \gg k$, the maximum and minimum values of the square root of the reflection coefficient and the corresponding values of d/λ are expressed approximately by simple equations derived from Eq. (2).[1] Therefore we can determine roughly n and k from the experimental curve, even if the condition $n \gg k$ is not satisfied. However, we have

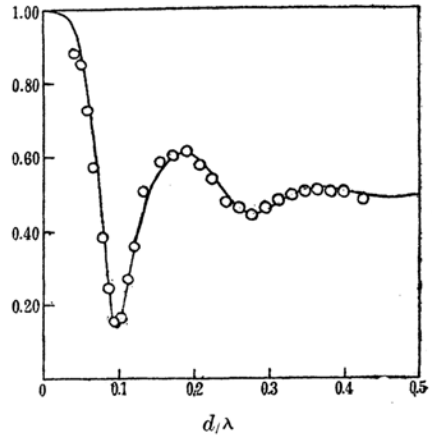

Fig. 4. The square root of the reflection coefficient of the methyl Alcohol layer of the thickness d/λ measured at 9°C and the calculated curve corresponding to $n=2.72$ and $k=0.78$.

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[15] Cf. T. Tamura, *Reports of the Radiation Chemistry Research Institute* (Tokyo Univ; in Japanese), **5**, 49 (1950).

prepared many calculated curves for values of n between 7.00 and 1.50 and of k between 2.00 and 0.10, and we compared the experimental curve with the calculated ones. Two examples of the calculated curves are shown in Figs. 4 and 5.

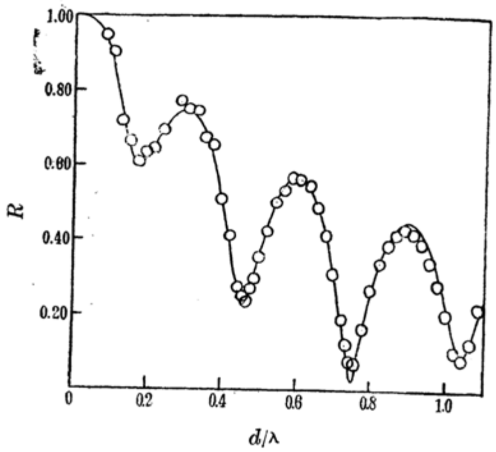

Fig. 5. The square root of the reflection coefficient of the *tert*-Butyl alcohol layer of the thickness d/λ measured at 26°C and the calculated curve corresponding to $n=1.685$ and $k=0.135$.

But the number of such calculated curves are not sufficient to determine the values of n and k accurately. We can choose the two nearest curves among the calculated ones. Now we choose a more suitable set of values of n and k, taking into account that the interval of d/λ corresponding to the two neighboring minimum points depends mainly upon the value of n and that the maximum and minimum values of R depend mainly on the value of k. By means of the interpolation method, we can determine more accurately the values of n and k respectively. Then we draw a curve with this set of n and k, and compare it once more with the experimental curve. If the experimental curve shows a deviation from the calculated one, we repeat the abovementioned procedure once more. Thus we can determine a more and more suitable set of n and k, and therefore ε' and ε''. In this experiment, we measured in many cases the standing-wave ratio until the thickness of the liquid layer became greater than the wavelength used. Therefore we could measure several maximum and minimum positions of R, as seen from Fig. 5.

Evaporation gives rise to an error in determining the thickness of liquid. To remove this effect, first we increase the volume of the liquid concerned in order to know the behaviour of the square root of the reflection coefficient, and then decreasing the thickness, we measure the standing-wave ratio very rapidly and accurately.

In a case when liquid shows the medium absorption in this microwave region as *tert*-butyl alcohol does, it is fairly easy to determine the maximum and minimum points of the square root of the reflection coefficient. Taking into account that the feature of the curve R *versus* d/λ depends markedly on a given set of n and k, we can compare the experimental curve with the calculated ones and determine accurately the set of n and k. The errors in determining the values

TABLE I

THE SQUARE ROOT OF THE REFLECTION COEFFICIENT R_e OF THE ETHYL ALCOHOL LAYER OF THE THICKNESS d/λ MEASURED AT 9°C AND THE CALCULATED ONE R_c CORRESPONDING TO $n=2.09$ AND $k=0.34$.

d/λ	R_e	R_c	d/λ	R_e	R_c
0.088	0.773	0.722	0.288	0.536	0.557
0.099	0.623	0.583	0.310	0.433	0.451
0.110	0.448	0.429	0.332	0.307	0.311
0.122	0.324	0.296	0.343	0.206	0.241
0.133	0.246	0.257	0.354	0.159	0.188
0.144	0.287	0.299	0.365	0.164	0.170
0.155	0.366	0.372	0.377	0.179	0.195
0.177	0.506	0.499	0.388	0.232	0.241
0.199	0.594	0.582	0.399	0.285	0.290
0.221	0.634	0.627	0.421	0.375	0.377
0.243	0.635	0.640	0.443	0.429	0.435
0.266	0.617	0.618	0.465	0.473	0.466

TABLE II

THE SQUARE ROOT OF THE REFLECTION COEFFICIENT R_e OF THE n BUTYL ALCOHOL LAYER OF THE THICKNESS d/λ MEASURED AT 18°C AND THE CALCULATED ONE R_c CORRESPONDING TO $n=1.72$ AND $k=0.165$

d/λ	R_e	R_c	d/λ	R_e	R_c
0.077	0.932	0.943	0.612	0.514	0.508
0.099	0.862	0.863	0.634	0.468	0.467
0.121	0.735	0.738	0.656	0.402	0.401
0.143	0.610	0.604	0.678	0.311	0.308
0.155	0.554	0.554	0.690	0.252	0.250
0.166	0.550	0.536	0.701	0.195	0.192
0.188	0.582	0.555	0.712	0.136	0.134
0.210	0.621	0.605	0.723	0.091	0.082
0.233	0.648	0.654	0.734	0.057	0.056
0.255	0.693	0.689	0.745	0.078	0.084
0.277	0.735	0.708	0.756	0.122	0.132
0.299	0.736	0.711	0.768	0.170	0.185
0.322	0.721	0.695	0.779	0.218	0.228
0.344	0.667	0.650	0.790	0.264	0.271
0.366	0.594	0.578	0.812	0.330	0.337
0.389	0.464	0.460	0.834	0.374	0.383
0.411	0.328	0.316	0.857	0.403	0.409
0.422	0.248	0.240	0.879	0.419	0.415
0.433	0.179	0.176	0.901	0.409	0.403
0.444	0.157	0.142	0.924	0.382	0.371
0.456	0.162	0.159	0.946	0.334	0.324
0.467	0.220	0.208	0.968	0.274	0.265
0.478	0.267	0.263	0.990	0.220	0.205
0.500	0.369	0.364	1.013	0.166	0.161
0.522	0.450	0.435	1.035	0.168	0.167
0.545	0.499	0.493	1.057	0.199	0.201
0.567	0.523	0.520	1.080	0.257	0.252
0.589	0.533	0.525			

of n and k by comparison are 0.2 percent for n and 2.0 percent for k. On the other hand, in a case when the liquid shows high absorption in this microwave region, as methyl alcohol does, the maximum and minimum points except for the first minimum point cannot be accurately recognized from the experimental curve and the large part of the curve is in the high reflection region as easily seen from Fig. 4. Further we must take into account that the standing-wave ratio measurement has the disadvantage of being unable to show the high reflection coefficient accurately. In this case the accuracy of determining the value of n is one percent.

Taking into account the errors due to the determination of the liquid thickness and of the wavelength, the accuracy in n is 0.8 percent for n-butyl- and isobutyl-alcohol. For methyl alcohol, ethyl alcohol and *tert*-butyl alcohol, showing the high vapour pressure, the accuracies may be 2.5, 1.6, and 1.6 percent, respectively.

The measured square roots of the reflection coefficients for various thicknesses of the liquid layer are plotted in Figs. 4 and 5 for methyl alcohol and *tert*-butyl alcohol, respectively. For ethyl, n-butyl and isobutyl alcohol, the experimental square roots of the reflection coefficients are listed in Table I, II, and III, together with the calculated ones for the experimentally determind values of n and k.

TABLE III

THE SQUARE ROOT OF THE REFLECTION COEFFICIENT R_e OF THE *iso*-BUTYL ALCOHOL LAYER OF THE THICKNESS d/λ MEASURED AT 23°C AND THE CALCULATED ONE R_c CORRESPONDING TO $n=1.70$ AND $k=0.160$.

d/λ	R_e	R_c	d/λ	R_e	R_c
0.072	0.930	0.959	0.585	0.524	0.527
0.095	0.880	0.889	0.608	0.515	0.522
0.117	0.797	0.776	0.630	0.494	0.493
0.139	0.613	0.641	0.652	0.438	0.440
0.162	0.570	0.552	0.675	0.351	0.357
0.173	0.550	0.543	0.697	0.256	0.256
0.184	0.554	0.551	0.719	0.144	0.139
0.195	0.585	0.570	0.730	0.093	0.083
0.217	0.635	0.619	0.741	0.064	0.045
0.240	0.685	0.665	0.753	0.074	0.072
0.262	0.696	0.692	0.764	0.123	0.122
0.284	0.686	0.711	0.775	0.167	0.173
0.307	0.705	0.711	0.797	0.245	0.261
0.329	0.678	0.691	0.820	0.308	0.333
0.351	0.631	0.647	0.842	0.357	0.380
0.373	0.543	0.570	0.864	0.389	0.407
0.396	0.451	0.451	0.886	0.404	0.416
0.418	0.310	0.309	0.909	0.408	0.406
0.429	0.233	0.238	0.931	0.359	0.380
0.440	0.181	0.180	0.953	0.340	0.333
0.452	0.148	0.154	0.976	0.248	0.272
0.463	0.176	0.175	0.998	0.188	0.209
0.474	0.209	0.221	1.020	0.147	0.158
0.496	0.317	0.330	1.043	0.145	0.150
0.518	0.405	0.410	1.065	0.185	0.185
0.541	0.462	0.474	1.087	0.220	0.234
0.563	0.501	0.511	1.110	0.277	0.283

The dielectric constant and the related quantities of some aliphatic alcohols are shown in Table IV.

TABLE IV

DIELECTRIC PROPERTIES OF SOME ALIPHATIC ALCOHOLS

Substance	Temp.	n	k	ε'	ε''
Methyl alcohol	9°C	2.72	0.78	6.79	4.24
Ethyl alcohol	8°C	2.09	0.34	4.25	1.42
n-Butyl alcohol	18°C	1.72	0.165	2.93	0.57
iso-Butyl alcohol	23°C	1.70	0.160	2.86	0.54
tert-Butyl alcohol	26°C	1.68_5	0.135	2.82	0.45

Conclusions

The dielectric constant and the loss factor of some aliphatic alcohols were measured by means of the free wave method developed by M. Yasumi. For liquids showing high boiling points, such as n-butyl and isobutyl alcohol, the accuracies of n and k are 0.8 and 2.0 percent, respectively. We should like to improve further the apparatus in the following points.

1) The accuracy in determining the thickness of the liquid layer must be increased.

2) Because we place the liquid layer on mercury in the free space, we can control the temperature within a limited range. But in order to study the dielectric properties of liquids, we must extend the temperature range. Also if the accuracy of measurement is further increased, the slight fall of temperature due to evaporation is a source of error. In the case of hygroscopic liquids, this effect may give rise to serious error.

3) It is necessary to make the radiation pattern more like the plane wave. By doing so, the error in fitting the experimental curve in the calculated curves will be decreased.

According to the plan described above, we are now improving the apparatus in order to increase the accuracy of measurement. We will postpone the detailed discussion of experimental results till later.

In conclusion, thanks are especially due to Dr. Masasi Yasumi for his guidance and to Prof. San-ichiro Mizushima for his kind advice and encouragement. The author also wishes to thank Mr. Yoshio Tsubahara who assisted him in constructing the electronic part of this apparatus, and to Mr. Tsurahide Cho and Mr. Takaaki Tamura who prepared the samples used in these experiments. The present work has been supported partly by the Scientific Research Grant from the Ministry of Educations.

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