Dielectric Properties of Monohalogenobenzenes in the Microwave Region

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The assumption of the local field plays an important rôle in the theory of the anomalous dispersion of a dielectric constant and the absorption of electric waves by a polar liquid.

Debye was the first to succeed in explaining theoretically the phenomena concerning the dielectric relaxation of polar liquids[1]. Debye's assumption for the local field explains inadequately the experimental results of dielectric constants, however. Nevertheless, the assumption of a single relaxation time seems to be at least approximately valid in the cases of many polar liquids from the experimental point of view[2].

Recently Yasumi and Komooka have derived a formula of the local field in liquids[3]. Applying the formula, they have shown that the validity of the assumption of a single relaxation time is justified in the case of polar liquids, which consist of molecules with a spherical shape and isotropic polarizability, and that the critical frequency ν_c is related to the relaxation time τ as follows:

$$2\pi\nu_c\tau=1$$

Thereafter, the formula for the local field has been extended to the case of liquids which consist of molecules with a ellipsoidal shape and anisotropic polarizability, and the formula for the static dielectric constant[4] and that for the Kerr constant of pure liquid[5] have been

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[1] P. Debye, "Polare Molekeln", Hirzel, Leipzig (1929).

[2] F. H. Müller, *Ergeb. exakt. Naturw.*, **17**, 164 (1938); A. Schallachmach, *Trans. Faraday Soc.*, **42A**, 180 (1946); C. H. Collie, J. B. Hasted and D. M. Ritson, *Proc. Phys. Soc.*, **60**, 145 (1948); J. B. Hasted, G. H. Haggis and P. Hutton, *Trans. Faraday Soc.*, **47**, 577 (1951); G. H. Haggis, J. B. Hasted and T. J. Buchanan, *J. Chem. Phys.*, **20**, 1452 (1952); J. A. Saxton, *Proc. Roy. Soc.*, **A213**, 473 (1952).

[3] M. Yasumi and H. Komooka, This Bulletin, **29**, 407 (1956).

[4] M. Yasumi, H. Okabayashi and H. Komooka, ibid., **31**, 402 (1958).

[5] H. Okabayashi, ibid., **34**, 1010 (1961).

derived. In the cases of liquid chloro-, bromo- and iodo-benzene, these formulae explain the experimental facts fairly well.

In the present work, the complex dielectric constants of liquid monohalogenobenzenes are measured in the microwave region; the paper's results are discussed on the basis of the formula of the local field derived by Yasumi and Komooka. The free wave method developed by Yasumi(6) and the waveguide method of Surber(7) are used.

Materials

Chloro- and bromo-benzene were fractionally distilled.

Iodobenzene was three times vacuum distilled.

	B. p., °C
Chlorobenzene	130.9
Bromobenzene	155.3
Iodobenzene	42.8 under the pressure of 3 mmHg.

Experimental

Free Wave Method. — This method has been theoretically developed in detail by Yasumi(6), and in his laboratory the dielectric properties of various liquids have been investigated in the microwave region(8-11).

In this work, the dielectric constant and the loss factor of halogenobenzenes were measured by the free wave method at the wavelength of 1.38 cm. The apparatus has been reported on in detail in a previous paper(11).

If R^2 is denoted as the reflection coefficient of a system consisting of a liquid layer of the thickness d on mercury, and λ is the wavelength of an electric wave in vacuo, the reflection coefficient is represented as follows:

$$R_2=\frac{\sinh^2\left(2\pi k\frac{d}{\lambda}+\frac{1}{2}\ln R_{12}\right)+\cos^2\left(2\pi n\frac{d}{\lambda}-\frac{\gamma}{2}\right)}{\sinh^2\left(2\pi k\frac{d}{\lambda}-\frac{1}{2}\ln R_{12}\right)+\cos^2\left(2\pi n\frac{d}{\lambda}+\frac{\gamma}{2}\right)} \tag{1}$$

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

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

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

$$\varepsilon'=n^2-k^2, \qquad \varepsilon''=2nk \tag{3}$$

The values of ε' and ε'' can be determined from the observed curve of R versus d/λ by the same way as described in the previous paper(11).

The observed values of R at different thicknesses of the liquid layer of chlorobenzene (at $t=13$°C and $\lambda=1.38$ cm.) are shown in Fig. 1, together with the calculated curve for the determined values of n and k.

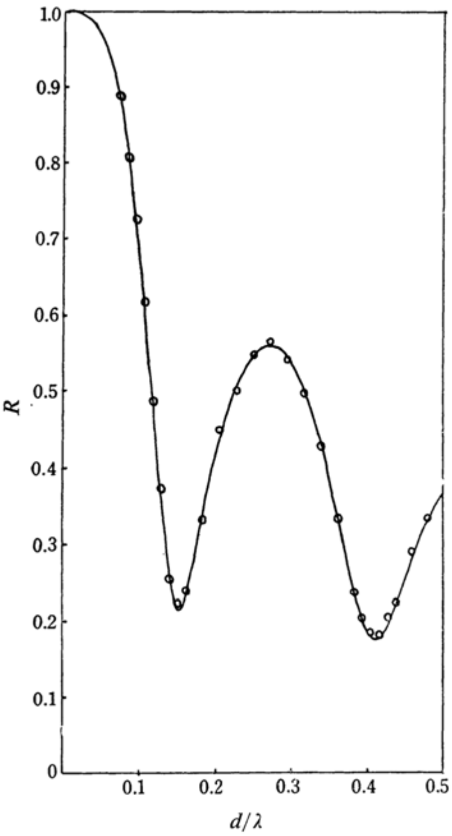

Fig. 1. The square root of the reflection coefficient of the chlorobenzene layer of the thickness d/λ measured at 13°C and the wavelength of 1.38 cm. and the calculated curve corresponding to $n=1.86$ and $k=0.36$.

The errors of ε' and ε'' are probably within ±1.5 and ±2.5% respectively.

Waveguide Method.—The dielectric constant and the loss factor at the wavelengths of 3.30 and 4.35 cm. were measured by means of the waveguide method. Each apparatus was similar to the one used by Crouch(12), by Smyth(13), or by Koizumi(14). A block diagram of the apparatus is shown in Fig. 2.

The directional coupler picks up the reflected wave from the liquid-filled waveguide cell. The reflected power P corresponding to a liquid layer of the thickness d can be known by the detector

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6) M. Yasumi, ibid., **24**, 53 (1951).

7) W. H. Surber, *J. Appl. Phys.*, **19**, 541 (1948).

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

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

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

11) H. Okabayashi, ibid., **28**, 312 (1955).

12) G. E. Crouch, *J. Chem. Phys.*, **16**, 364 (1948).

13) H. L. Lacquer and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4097 (1948).

14) N. Koizumi, *J. Chem. Phys.*, **27**, 625 (1957).

TABLE I. THE OBSERVED VALUE OF P/P_{∞} FOR LIQUID BROMOBENZENE LAYER OF THE THICKNESS d/λ ($t=25^{\circ}\mathrm{C}$ AND $\lambda=3.29$ cm.) AND THE CALCULATED VALUE CORRESPONDING TO $n_{\mathrm{w}}=1.898$ AND $k_{\mathrm{w}}=0.363$

d/λ	$(P/P_{\infty})_{\mathrm{obs}}$	$(P/P_{\infty})_{\mathrm{calcd}}$
0.0169	2.094	2.215
0.0206	1.967	2.064
0.0254	1.882	1.961
0.0290	1.863	1.932
0.0339	1.878	1.936
0.0393	1.927	1.978
0.0454	2.012	2.052
0.0877	2.626	2.624
0.0937	2.689	2.683
0.0998	2.744	2.735
0.1058	2.789	2.778
0.1119	2.822	2.814
0.1191	2.852	2.846
0.1246	2.864	2.861
0.1300	2.870	2.869
0.1355	2.870	2.869
0.1409	2.864	2.859
0.1482	2.834	2.831
0.1542	2.798	2.794
0.1602	2.744	2.743
0.1633	2.714	2.710
0.1663	2.671	2.671
0.2540	0.297	0.295
0.2558	0.272	0.272
0.2576	0.251	0.252
0.2594	0.236	0.235
0.2618	0.219	0.218
0.2643	0.207	0.207
0.2673	0.203	0.202
0.2691	0.204	0.203
0.2721	0.212	0.211
0.2739	0.220	0.219
0.2757	0.231	0.230
0.2782	0.248	0.249
0.2812	0.278	0.277
0.2842	0.312	0.310
0.3628	1.418	1.413
0.3689	1.462	1.456
0.3779	1.513	1.505
0.3828	1.529	1.523
0.3882	1.543	1.537
0.3955	1.548	1.545
0.4009	1.545	1.544
0.4088	1.533	1.530
0.4112	1.526	1.523
0.4172	1.504	1.501
0.4233	1.475	1.471
0.4263	1.457	1.453
0.4293	1.437	1.434
0.5019	0.800	0.805
0.5049	0.785	0.788
0.5079	0.770	0.774
0.5110	0.756	0.760
0.5140	0.745	0.749
0.5176	0.734	0.739
0.5212	0.726	0.731
0.5249	0.722	0.726
0.5285	0.721	0.724
0.5321	0.722	0.724
0.5358	0.724	0.727
0.5412	0.731	0.736
0.5472	0.747	0.751
0.5533	0.770	0.772
0.5593	0.793	0.796
0.6259	1.108	1.106
0.6349	1.132	1.130
0.6398	1.143	1.140
0.6446	1.150	1.148
0.6513	1.157	1.156
0.6567	1.161	1.159
0.6603	1.161	1.160
0.6658	1.161	1.159
0.6718	1.157	1.155
0.6773	1.149	1.149
0.6833	1.139	1.140
0.6894	1.128	1.128
0.6954	1.114	1.115
0.7649	0.935	0.937
0.7698	0.928	0.930
0.7746	0.922	0.924
0.7819	0.914	0.918
0.7891	0.913	0.915
0.7940	0.913	0.915
0.7988	0.915	0.916
0.8042	0.917	0.918
0.8103	0.920	0.922
0.8163	0.927	0.928
0.8194	0.929	0.931
0.8224	0.932	0.935

system. When the thickness of the layer is changed, P is also changed, and the curve, P versus d/λ, is obtained. By an analysis of the curve thus obtained, the values of ε' and ε'' of the liquid can be determined.

Reflex klystrons of the types Raytheon RK5976 and Raytheon 2K25 were used as the oscillator tubes at the wavelengths of 4.35 and 3.30 cm. respectively.

The plunger in the liquid-filled waveguide is of the open circuit-terminated type and is constructed of a teflon block whose length is a quarter of the

TABLE II. THE OBSERVED VALUE OF P/P_{∞} FOR LIQUID IODOBENZENE LAYER OF THE THICKNESS d/λ ($t=25°\text{C}$ AND $\lambda=4.347$ cm.) AND THE CALCULATED VALUE CORRESPONDING TO $n_{\text{w}}=1.794$ AND $k_{\text{w}}=0.259$

d/λ	$(P/P_{\infty})_{\text{obs}}$	$(P/P_{\infty})_{\text{calcd}}$
0.0242	3.554	3.566
0.0260	3.489	3.500
0.0292	3.396	3.413
0.0320	3.352	3.358
0.0348	3.320	3.325
0.0366	3.309	3.312
0.0421	3.302	3.303
0.0439	3.309	3.309
0.0458	3.316	3.318
0.0508	3.356	3.358
0.0550	3.403	3.403
0.0596	3.453	3.458
0.0642	3.514	3.520
0.1037	4.020	4.009
0.1079	4.061	4.047
0.1125	4.093	4.084
0.1171	4.124	4.116
0.1207	4.142	4.137
0.1244	4.161	4.156
0.1276	4.179	4.170
0.1304	4.188	4.179
0.1373	4.197	4.192
0.1428	4.192	4.192
0.1493	4.174	4.179
0.1539	4.156	4.159
0.1585	4.133	4.131
0.1631	4.097	4.094
0.1677	4.043	4.041
0.2757	0.072	0.070
0.2776	0.044	0.045
0.2803	0.015	0.019
0.2831	0.001	0.004
0.2854	0.000	0.0006
0.2886	0.008	0.008
0.2927	0.035	0.037
0.2964	0.078	0.079
0.3010	0.154	0.151
0.3838	1.960	1.968
0.3953	2.083	2.088
0.4031	2.142	2.144
0.4082	2.167	2.169
0.4123	2.183	2.183
0.4183	2.192	2.192
0.4264	2.183	2.185
0.4307	2.172	2.172
0.4344	2.153	2.156
0.4455	2.069	2.078
0.4574	1.948	1.949
0.4666	1.814	1.818
0.5471	0.464	0.460
0.5526	0.431	0.430
0.5567	0.418	0.417
0.5604	0.413	0.412
0.5641	0.412	0.414
0.5673	0.417	0.419
0.5705	0.426	0.429
0.5769	0.458	0.461
0.5815	0.490	0.492
0.5861	0.526	0.529
0.5907	0.566	0.571
0.6620	1.321	1.322
0.6730	1.392	1.388
0.6795	1.420	1.411
0.6850	1.433	1.434
0.6892	1.446	1.444
0.6947	1.452	1.451
0.6961	1.454	1.451
0.7002	1.454	1.453
0.7057	1.452	1.449
0.7099	1.443	1.444
0.7149	1.433	1.431
0.7241	1.402	1.398
0.7310	1.368	1.365
0.7402	1.311	1.311
0.8115	0.809	0.804
0.8207	0.774	0.770
0.8276	0.753	0.752
0.8313	0.750	0.746
0.8345	0.744	0.742
0.8372	0.743	0.741
0.8428	0.741	0.742
0.8487	0.748	0.747
0.8552	0.759	0.758
0.8621	0.776	0.777
0.8713	0.808	0.809

wavelength in the teflon-filled waveguide. The mica sheet of the thickness of about 3/100 mm. is inserted between the liquid cell and the waveguide connected to it in order to separate them. Two attenuators decrease the power level of the wave, which propagates towards the sample, about 30 db in order to loose the coupling between the klystron oscillator and the waveguide cell, because the reflection coefficient of the liquid-filled cell varies from unity to zoro.

The temperature of the liquid sample was controlled by water which circulated in the jacket surrounding the waveguide system and the thermostat, the fluctuation of the temperature was within ±0.1°C.

Before the liquid sample was poured into the

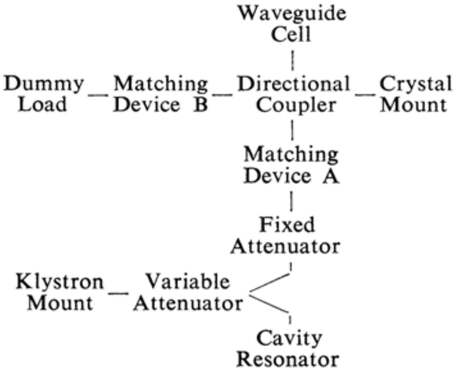

Fig. 2. The block diagram of the apparatus by the waveguide method.

waveguide cell, the following adjustments were made: After the movable dummy load of about 1.01 V. S. W. R. was inserted instead of the plunger in the waveguide cell, the matching device B (see Fig. 2) was adjusted so as to minimize the variation in the reading of the detector when the position of the dummy load was changed. After the plunger was set up in the waveguide cell, the matching device A (see Fig. 2) was adjusted so as to minimize the variation in the reading of the detector when the position of the plunger was changed.

If the effect of the mica sheet can be ignored, the reflection coefficient R_{w}^2 of the liquid layer in the waveguide cell has the following expression[*1]:

$$R_{\mathrm{w}}^2=\frac{\sinh^2\left(2\pi k_{\mathrm{w}}\frac{d}{\lambda}+\frac{1}{2}\ln R_{\mathrm{w}12}\right)+\sin^2\left(2\pi n_{\mathrm{w}}\frac{d}{\lambda}-\frac{\gamma_{\mathrm{w}}}{2}\right)}{\sinh^2\left(2\pi k_{\mathrm{w}}\frac{d}{\lambda}-\frac{1}{2}\ln R_{\mathrm{w}12}\right)+\sin^2\left(2\pi n_{\mathrm{w}}\frac{d}{\lambda}+\frac{\gamma_{\mathrm{w}}}{2}\right)} \tag{4}$$

In this case $R_{\mathrm{w}12}$ and γ_{w} are related to n_{w} and k_{w} as follows:

$$R_{\mathrm{w}12}^2=\frac{(n_{\mathrm{w}}-n_{\mathrm{w}1})^2+k_{\mathrm{w}}^2}{(n_{\mathrm{w}}+n_{\mathrm{w}1})^2+k_{\mathrm{w}}^2}$$

$$\tan\gamma_{\mathrm{w}}=\frac{2n_{\mathrm{w}1}k_{\mathrm{w}}}{n_{\mathrm{w}}^2-n_{\mathrm{w}1}^2+k_{\mathrm{w}}^2}$$

$$n_{\mathrm{w}1}=\left\{1-\left(\frac{\lambda}{\lambda_{\mathrm{c}}}\right)^2\right\}^{1/2} \tag{5}$$

in which λ_{c} is the cut-off wavelength characteristic of the waveguide. ε' and ε'' have the following relationship to n_{w} and k_{w}:

$$\varepsilon'=n_{\mathrm{w}}^2-k_{\mathrm{w}}^2+(\lambda/\lambda_{\mathrm{c}})^2,\quad \varepsilon''=2n_{\mathrm{w}}k_{\mathrm{w}} \tag{6}$$

If the reading of the detector system of the apparatus is proportional to the square of the field strength, it is also proportional to the reflection coefficient of the liquid layer in the waveguide. As the standard of the power, the power P_∞ for the liquid layer of infinite thickness is taken.

In this work, the values of n_{w} and k_{w}, and therefore ε' and ε'', were determined in the following way: Near the maximum and minimum points of the curve, P/P_∞ versus d/λ, the values of the power P were measured at short intervals. In Tables I and II some examples of the observed values of P/P_∞ are shown. The value of n_{w} was determined roughly from the separations of the maximum points. Next, the value of k_{w} was roughly determined from the values of P/P_∞ at the maximum points. Finally, the values of n_{w} and k_{w} were chosen in order to fit the observed values of P/P_∞ at different thicknesses of the liquid layer in the waveguide.

Various factors may contribute to the experimental error. One of the sources of error may be the disturbance of the wave by the mica sheet. This sheet forms a multiple layer with the liquid layer and the teflon-block in the waveguide[*2]. The effect can be checked by the theoretical calculation of the reflection coefficient of a multiple layer placed on a metal. The theoretical calculation shows that the effect of the mica sheet is negligible at the present stage of the accuracy.

When the values of n_{w} and k_{w} were determined, the value of P/P_∞ at the first minimum point was not taken into account[*3].

TABLE III. DIELECTRIC PROPERTIES OF SOME HALOGENOBENZENES OBSERVED BY THE FREE WAVE METHOD

Substance	Temp. °C	λ cm.	n	k	ε'	ε''
Chlorobenzene	26	3.24[1]	2.18	0.33	4.64	1.44
	14	3.24[1]	2.16	0.365	4.54	1.58
	13	1.38	1.86	0.36	3.33	1.34
Bromobenzene	23	1.39	1.75_5	0.28_5	3.00	1.00

1) M. Yasumi and M. Shirai, to be published.

TABLE IV. DIELECTRIC PROPERTIES OF SOME HALOGENOBENZENES OBSERVED BY THE WAVEGUIDE METHOD*

Substance	Temp. °C	λ cm.	n_{w}	k_{w}	ε'	ε''
Chlorobenzene	25	3.295	2.06_5	0.345	4.66	1.43
		4.347	2.16_4	0.287	4.99	1.24
	40	3.295	2.06_4	0.297	4.69	1.22
		4.347	2.14_2	0.242	4.92	1.04
Bromobenzene	25	3.295	1.89_8	0.363	3.99	1.38
		4.347	2.01_6	0.328	4.35	1.32
	40	3.295	1.92_0	0.332	4.09	1.27
		4.347	2.02_5	0.288	4.41	1.17
Iodobenzene	25	3.295	1.68_5	0.253	3.29	0.85
		4.347	1.79_4	0.259	3.54	0.93

* The values of λ_{c} for the apparatus at the wavelengths of 3.295 and 4.347 cm. are 4.58_0 and 6.97_0 cm. respectively.

[*1] Yasumi's theoretical treatment concerning the free wave method can be conveniently applied to the waveguide method with a few modifications. For example, n_{w} and k_{w} in this case correspond to n and k, and the refractive index of vacuum (which is unity) should be replaced by $n_{\mathrm{w}1}(\neq 1)$. ε'' is related to n_{w} and k_{w} by Eq. 6.

[*2] The length of the teflon block is a quarter of the wavelength in the teflon-filled waveguide. In this work the samples with high absorption coefficients were tested. Therefore, the error due to the teflon block seems to be negligible.

[*3] The details will be reported on elsewhere.

The errors of ε' and ε'' were within ±1%.

The obtained values of ε' and ε'' of liquid monohalogenobenzenes are tabulated in Tables III and IV. On the other hand, Yasumi and Shirai have measured the complex dielectric constant of liquid chlorobenzene by the free wave method at the wavelength of 3.24 cm. These values are shown in Table III for comparison. The results by the waveguide method shows an fair agreement with those obtained by the free wave method.

Theoretical Discussion

A molecule of monohalogenobenzene is rigid, and each principal axis of its polarizability ellipsoid coincides with each of the principal axes of the molecular ellipsoid. In such a case, the component of the local field $\vec{F}$ has the following expression[4]:

$$\left.\begin{aligned} F_i&=\left(1-\frac{\varphi_i\alpha_i}{v}\right)^{-1}\left(E_i\mathrm{e}^{i\omega t}+\frac{\varphi_i\mu_{0i}}{v}\right)\\ &=\gamma_i\left(E_i\mathrm{e}^{i\omega t}+\frac{\varphi_i\mu_{0i}}{v}\right)\\ \varphi_i&=2\pi a_1a_2a_3\\ &\times\int_0^\infty\frac{\mathrm{d}u}{(a_i^2+u)\sqrt{(a_1^2+u)(a_2^2+u)(a_3^2+u)}}\end{aligned}\right\}\quad(7)$$

in which $\vec{E}\mathrm{e}^{i\omega t}$ is the field strength in the medium, ω is the angular frequency of an applied field, $\vec{\mu}_0$ is the permanent dipole moment. α_i is the principal component of the polarizability tensor along the principal axis of the molecular ellipsoid, v is molecular volume, and $2a_i$ is the length of the principal axis of the molecular ellipsoid.

Perrin[15] treated the dielectric relaxation of a polar liquid consisting of ellipsoidal molecules from the point of view of hydrodynamics, and derived a partial differential equation which determines the distribution function of dipole orientation. The equation of Perrin will be applied to Eq. 7.

If the potential energy of a dipole under the influence of the electric field is denoted by U, we have

$$U=-\left(\frac{1}{2}\sum\alpha_iF_i^2+\sum\mu_{0i}F_i\right)\qquad(8)$$

If only the term proportional to E is retained, the torques L_i about each principal axis of the molecular ellipsoid have the following expressions:

$$\left.\begin{aligned} L_1&=E\mathrm{e}^{i\omega t}(\mu_{02}\gamma_2{}^2\zeta_3-\mu_{03}\gamma_3{}^2\zeta_2)\\ L_2&=E\mathrm{e}^{i\omega t}(\mu_{03}\gamma_3{}^2\zeta_1-\mu_{01}\gamma_1{}^2\zeta_3)\\ L_3&=E\mathrm{e}^{i\omega t}(\mu_{01}\gamma_1{}^2\zeta_2-\mu_{02}\gamma_2{}^2\zeta_1)\end{aligned}\right\}\quad(9)$$

in which ζ_1, ζ_2 and ζ_3 are the direction cosines of the electric field $\vec{E}$ with respect to the principal axes of molecular ellipsoid respectively.

Inserting Eqs. 9 into Perrin's equation, we have the following expression of the probability function f as the approximate solution of the differential equation:

$$f=f_0+f_0\frac{E\mathrm{e}^{i\omega t}}{kT}\sum\frac{\mu_{0i}\gamma_i{}^2}{1+i\omega\tau_i}\zeta_i\qquad(10)$$

f_0 denotes the distribution function when no electric field is applied. τ_i is the relaxation time and is related to the viscosity coefficient of liquid η as follows:

$$\left.\begin{aligned} \tau_i&=\frac{C_{jk}}{2kT}\\ \frac{2}{C_{jk}}&=\frac{1}{C_j}+\frac{1}{C_k}\\ C_i&=\frac{32\pi^2}{3}a_1a_2a_3\frac{\left(\frac{a_j}{a_1}\right)^2+\left(\frac{a_k}{a_1}\right)^2}{\left(\frac{a_j}{a_1}\right)^2\varphi_j+\left(\frac{a_k}{a_1}\right)^2\varphi_k}\eta\end{aligned}\right\}\quad(11)$$

The total electric moment of the molecule $\vec{\mu}$ is the sum of the permanent dipole moment and the induced dipole moment.

$$\mu_i=\mu_{0i}+\alpha_iF_i\qquad(12)$$

If the component of $\vec{\mu}$ along the direction $\vec{E}$ is denoted by μ_E, and the statistical mean value of μ_E is denoted by $\langle\mu_E\rangle$, we have

$$\mu_E=\sum\mu_i\frac{E_i}{E}=\sum\gamma_i(\alpha_iE\mathrm{e}^{i\omega t}+\mu_{0i})\frac{E_i}{E}\qquad(13)$$

and

$$\langle\mu_E\rangle=\frac{\int f\mu_E\mathrm{d}\Omega}{\int f\mathrm{d}\Omega}\qquad(14)$$

in which $\mathrm{d}\Omega$ is an elementary solid angle.

Inserting Eqs. 10 and 13 into Eq. 14, we have

$$\langle\mu_E\rangle=\left(\frac{\sum\alpha_i\gamma_i}{3}+\frac{1}{3kT}\sum\frac{\mu_{0i}\gamma_i{}^3}{1+i\omega\tau_i}\right)E\mathrm{e}^{i\omega t}\qquad(15)$$

The complex dielectric constant ε is related to $\langle\mu_E\rangle$ by the following equation:

$$(\epsilon-1)E\mathrm{e}^{i\omega t}=4\pi N_c\langle\mu_E\rangle\qquad(16)$$

in which N_c is the number of molecules in a unit volume.

Accordingly, the dielectric constant ε' and the loss factor ε'' have the following expressions:

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[15] F. Perrin, *J. phys.*, 5, 497 (1934).

$$\left.\begin{aligned} \varepsilon' &= \varepsilon_\infty + \frac{4\pi N_c}{3kT}\sum\frac{\mu_{0i}{}^2\gamma_i{}^3}{1+\omega^2\tau_i{}^2} \\ \varepsilon'' &= \frac{4\pi N_c}{3kT}\sum\frac{\mu_{0i}{}^2\gamma_i{}^3}{1+\omega^2\tau_i{}^2}\,\omega\tau_i \\ \varepsilon_\infty &= 1+4\pi N_c\sum\frac{\alpha_i\gamma_i}{3} \end{aligned}\right\} \quad (17)$$

Equations 17 show that generally there are three relaxation times.

If the direction of the permanent dipole moment coincides with one of the principal axes of the molecular ellipsoid, the Eqs. 17 are simplified as follows:

$$\left.\begin{aligned} \varepsilon' &= \varepsilon_\infty + \frac{\varepsilon_0-\varepsilon_\infty}{1+\omega^2\tau^2} \\ \varepsilon'' &= \frac{\varepsilon_0-\varepsilon_\infty}{1+\omega^2\tau^2}\,\omega\tau \end{aligned}\right\} \quad (18)$$

in which ε_0 is the static dielectric constant of a polar liquid. It is assumed that the polarizability is independent of frequency.

In Tables V and VI the values of ε_∞ and τ obtained from the experimental values of the complex dielectric constant are tabulated, together with the value of the static dielectric constant ε_0 and that of the square of the refractive index n_D^2.

In Table VII the values of ε_∞ evaluated from the sum of the electronic polarization P_E and the atomic polarization P_A are tabulated. It is assumed that the Lorentz-Lorenz law is valid.

The values of ε_∞ evaluated from the experimental values of ε' and ε'' at different wavelengths coincide with each other within the limits of experimental error.

Yasumi, Shirai and Mizushima[10] hava measured the dielectric constant and the loss factor of liquid aliphatic alcohols at the wavelength of 3.24 cm. and have shown that the value of ε_∞ evaluated according to Eqs. 18 is considerably larger than the square of the refractive index for the sodium D line (n_D^2). This interesting result has been confirmed by the measurements at the wavelength of 1.38 cm.[11] However, in the case of liquid monohalogenobenzene the value of ε_∞ is much closer to the value of n_D^2 and, moreover, is almost equal to the value ε_∞ evaluated from the value of (P_E+P_A).

TABLE V. THE VALUES OF ε_∞ AND τ OF HALOGENOBENZENES EVALUATED FROM THE EXPERIMENTAL VALUES OF ε' AND ε'' BY THE FREE WAVE METHOD

Substance	Temp. °C	λ cm.	ε_0	n_D^2	ε_∞	$\tau\times10^{11}$ sec.
Chlorobenzene	26[1]	3.24	5.61[2]	2.32	2.50±0.15	1.16
	14[1]	3.24	5.86[2]	2.33	2.65±0.10	1.44
	13	1.38	5.89[2]	2.33	2.63±0.08	1.40
Bromobenzene	23	1.39	5.42[2]	2.43	2.59±0.07	1.80

1) M. Yasumi and M. Shirai, to be published.
2) W. A. Hestone, E. T. Hennelly and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 207(1950).

TABLE VI. THE VALUES OF ε_∞ AND τ OF HALOGENOBENZENE EVALUATED FROM THE EXPERIMENTAL VALUES OF ε' AND ε'' BY THE WAVEGUIDE METHOD

Substance	Temp. °C	λ cm.	ε_0	n_D^2	ε_∞	$\tau\times10^{11}$ sec.
Chlorobenzene	5[1]	3.25	6.06[2]	2.35	2.59±0.05	1.62
	25	3.30	5.63[2]	2.32	2.55±0.10	1.19
		4.35			2.6 ±0.2	1.19
	40	3.30	5.31[2]	2.29	2.3 ±0.2	0.89
		4.35			2.2 ±0.3	0.84
Bromobenzene	5[1]	3.25	5.68[2]	2.46	2.69±0.04	2.37
	25	3.30	5.39[2]	2.43	2.63±0.03	1.77
		4.35			2.67±0.06	1.81
	40	3.30	5.18[2]	2.40	2.61±0.05	1.51
		4.35			2.63±0.09	1.52
Iodobenzene	25	3.30	4.62[3]	2.62	2.75±0.03	2.75
		4.35			2.74±0.03	2.68

1) T. Kato and H. Okabayashi, to be published.
2) W. A. Hestone, E. T. Hennelly and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 207(1950).
3) A. Audsley and F. R. Goss, *J. Chem. Soc.*, **1942**, 497; C. R. K. Murty, *J. Sci. Ind. Research (India)*, **18B**, 268 (1959).

TABLE VII. THE VALUES OF ε_∞ AT 25°C EVALUATED FROM THE VALUE OF (P_E+P_A)

Substance	(P_E+P_A)[1] cc.	ε_∞
Chlorobenzene	34.9	2.56
Bromobenzene	35.6	2.53
Iodobenzene	41.4	2.76

1) C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, **1954**, 1577.

From Tables V and VI the validity of Eqs. 18 seems to be justified in the cases of liquid monohalogenobenzenes; i. e. the dielectric relaxation is explained by the single relaxation time, and ε_∞ in Eqs. 18 has a value almost the same as the value of n_D^2.

According to Fqs. 11, the effective volume of a molecule v_e for the molecular rotation can be evaluated from the observed relaxation time if the ratios of the lengths of the principal axes of the molecular ellipsoid are known. In Table VIII the values of the effective volume v_e of the molecules at 25°C are shown, together with those of the volume $v_{(\text{van der Waals})}$ of the molecular ellipsoid (the model which is assumed in order to determine the axial ratios). Also, the values of the molecular volume v

TABLE VIII. THE EFFECTIVE VOLUME v_e OF A MOLECULE, THE VOLUME $v_{(\text{van der Waals})}$ OF THE ASSUMED MOLECULAR ELLIPSOID AND THE MOLECULAR VOLUME v EVALUATED FROM THE MOLAR VOLUME AT 25°C

Substance	Chlorobenzene	Bromobenzene	Iodobenzene
$\tau\times10^{11}$, sec.	1.19	1.79	2.72
Assumed axial ratio	1 : 0.77 : 0.43	1 : 0.75 : 0.45	1 : 0.69 : 0.45
$\eta\times10^3$ (poise)[1]	7.53	10.8	15.3
v_e, Å^3	15.1	15.7	17.4
$v_{(\text{van der Waals})}$, Å^3	107	117	135
v, Å^3	170	175	186
$v_e/v_{(\text{van der Waals})}$	0.141	0.133	0.131
v_e/v	0.089	0.090	0.094

1) K. Shiba, "Butsuri Jōsūhyō", Iwanami-shoten (1947).

evaluated from the molar volume are shown for reference.

The value of v_e is only about 13% of the value of $v_{(\text{van der Waals})}$. The reason why the value of v_e is so small is obscure as yet.

Summary

The dielectric constants and the loss factors of liquid monohalogenobenzenes were measured in the microwave region by the free wave method and the waveguide method. The experimental results were discussed on the basis of the formula of the local field previously proposed. In the cases of liquid monohalogenobenzenes, the experimental facts can be explained by a single relaxation time.

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