

in a later paper and of 1.27 for λ_t gives $\lambda_m = 2.51$ cm. for *n*-propyl bromide at 1° and 2.16 for *n*-butyl bromide at 55° in fair agreement with the values 2.34 and 2.18 cm. calculated by means of an equation based on the Debye theory⁹

$$\lambda_m = \frac{\lambda_0}{2} \frac{(\epsilon_0 - \epsilon_\infty)}{\epsilon''} + \frac{\lambda_0}{2} \left[\left(\frac{\epsilon_0 - \epsilon_\infty}{\epsilon''} \right)^2 - 4 \right]^{1/2} \quad (13)$$

in which λ_0 , the free space wave length, is 1.27 cm. However, a similar analysis of loss tangent values at 3.2 cm. wave length calculated from measurements to be reported in a later paper leads to rough values of λ_m for *n*-butyl bromide at 1°, *n*-amyl at 25° and *n*-hexyl at 55° about twice as large as those given by equation (13). To obtain equation (13), $(\epsilon_0 + 2)/(\epsilon_\infty + 2)$ has been eliminated in accordance with the Onsager theory.¹⁰ If this approximation is not made, the agreement of the calculated values with those estimated from the loss tangent curves is worse. These loss factor curves depend particularly upon the wave length at which they are obtained, upon the molecular dipole moments and the concentration of dipoles, which decreases with increasing molecular size, and upon the molecular sizes and the viscosities of the liquids, which increase with increasing molecular size. They will be examined in detail

(10) Onsager, *THIS JOURNAL*, **58**, 1486 (1936).

in connection with the results of solution measurements now being carried out.

The significance of the experimental data in the present paper will be considered in the third paper of this series, in which additional material will be presented.

Summary

A method is described for the measurement of the dielectric constant and loss of high loss liquids by means of the variation in the reflection coefficient of a uniform dielectric layer as the depth of the layer is varied. The experimental procedure for measurement at a wave length of 1.27 cm., method of calculation, and errors are discussed.

Values are given for the dielectric constants and loss factors at temperatures from 1 to 55° of ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *s*-butyl, *t*-butyl, *n*-amyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-nonyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl and *n*-hexadecyl bromides, and *n*-octyl chloride, *n*-octyl iodide, *n*-dodecyl chloride, cyclohexyl bromide, chlorobenzene, bromobenzene, α -chloronaphthalene, α -bromonaphthalene, ethylene chloride, ethylene bromide and tetramethylene chloride.

The loss tangents of the straight-chain bromides give a smooth curve when plotted against chain length.

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Microwave Absorption and Molecular Structure in Liquids. II. Measurement in Organic Halides at 3.22 Cm. Wave Length¹

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Preliminary measurements of the dielectric constants and loss factors at 9.72 cm. wave length of a considerable number of organic molecules² showed that the relaxation times of the molecules increased with their size, as required by the Debye theory of anomalous dielectric dispersion,³ and also increased with the extent of their departure from spherical form. These measurements combined with unpublished measurements carried out in this laboratory by Dr. M. Magat and Dr. W. C. Schneider indicated an almost linear dependence of the relaxation time upon the number of carbon atoms in a straight-chain molecule with a possibility of an approach toward constancy of relaxation time in the long-chain molecules. Further measurements by one of the present authors with the 9.72 cm. apparatus indicated some deterioration in the equipment during the war period and

suggested that improved accuracy could be obtained by the employment of newly developed apparatus and methods.

Apparatus and Method

In the original 9.72-cm. apparatus² a moving plunger effectively pushed a standing wave pattern past a fixed probe. This pattern was the result of the superposition of the fixed reflection at the air-dielectric interface upon the varying one from the moving plunger, which, in addition, had been transformed through a varying length of liquid and through a solid dielectric plug forming the bottom of the cell. The observed pattern was not symmetrical, its asymmetry depending on the position of the probe and being least whenever the probe was located at a voltage node from the first reflection. If by suitable matching or transforming methods the first reflection could be completely eliminated, a very simple pattern would result. An attempt was made to use a double stub tuner with a coaxial line for this transformation. With an effectively infinite dielectric column, the tuner was varied until a slotted line on the input

(1) This research was partially supported by the Office of Naval Research.

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(2) Conner and Smyth, *THIS JOURNAL*, **65**, 382 (1943).

(3) Debye, "Polar Molecules," The Chemical Catalog Co., New York N. Y., 1929, Chap. V.

side showed unity standing wave ratio. Then, keeping the probe at an arbitrary position, a symmetrical pattern was obtained upon varying the liquid length. Moving the probe to another position would produce a similar pattern and the envelope of all these patterns would be a smooth curve. The decrease of the envelope, however, was found to be more than exponential, since the match obtained by the double stub tuner was only uni-directional and the returning wave would not go into the air-line completely but be reflected back into the dielectric. On the other hand, the curves were sufficiently symmetrical to give the same wave length from successive maximum and minimum positions. If the match was disturbed, as was ordinarily the case in the original apparatus, the wave lengths from the positions of the maxima were either greater or less, depending on the probe position, than those from the positions of the minima. However, the average from maxima and minima should be very close to the results obtained with the matched setup.

An attempt was made to match out the first reflection with a wave guide setup at 3 cm., but it was found impossible to obtain such a match either with a double slug tuner or with a movable screw tuner.

An entirely different approach which, instead of measuring standing wave ratios, involved the determination of the reflected energy only was suggested by Dr. W. Van B. Roberts. The apparatus involved employed circular wave guides and obtained the directional coupling effect through quarter-wave plates which changed the linear polarization of the outgoing radiation into circular polarization and polarized the returning circularly polarized radiation again linearly, its plane of polarization now being at right angles to the incident one.⁴ A value of 2.282 was found for the dielectric constant of benzene at room temperature which is in good agreement with the accepted value of 2.276 at 25°. ⁵ Unfortunately, difficulties arose due to multiple reflections at the polarizing plate, as well as due to the production of elliptical polarization upon reflection from a lossy dielectric; hence, the apparatus was abandoned in favor of one with a rectangular wave guide system for measurements at 3 cm. wave length.

The apparatus finally employed for the work at 3 cm. wave length was very similar to that described in the first paper⁶ of this series. The oscillator was part of a test set TS-120/UP⁷ and consisted of a 723A/B reflex tube which could produce continuous, pulsed or square-wave modulated radio-frequency power in the X-band or 10,000 megacycle region. Two built-in attenuators allowed variation of the output power of the test set from about 10 to 10⁻⁴ milliwatts and a resonant

cavity frequency meter, calibrated from 9285 to 9470 megacycles, measured the output frequency to 0.5 megacycle. The only change made in the test set was to introduce a variable resistance into the square-wave producing multivibrator so that it was possible to adjust the modulating frequency to any value in the neighborhood of 1000 cycles.

From the test set the radiation was guided through a standard X-band wave guide (1" × 1/2") around a right-angle bend past a fixed probe and a directional coupler through a mica window into the cell, where it was reflected from a micrometer driven plunger. The fraction of the reflected energy taken out in the directional coupler was rectified by an IN-23 crystal, which was mounted on the coupler, and then carried through a shielded cable to a Hazeltine Model 1052-A audio amplifier,⁸ tuned sharply to 1000 cycles.

Since only narrow-band two-hole directional couplers were available for use with the X-band equipment, fairly exact frequency adjustment was required for optimum directivity. The coupler employed functioned best at 9310 ± 20 megacycles, its coupling attenuation was about 20db and its directivity lay between 20 and 30db, which meant that it sampled 0.01 of the power traveling back toward the generator and between 0.0001 and 0.00001 of the power flowing in the opposite direction.

The mica window had to be installed after thin Teflon windows were found to be too flexible. It was made thin enough (0.001") so that its effects were negligible at the wave length employed. This avoided the use of a matching diaphragm to compensate for the reflections from the window. Whether or not one was justified in neglecting the effect of the mica window could be determined simultaneously with the directivity of the coupler and the smoothness or lack of undesired reflections of the whole wave guide system, including the right-angle bend and the last attenuator, by observing how small the variation in the output from the directional coupler was when the plunger was moved back and forth in the air-filled cell, once with the mica window in place and once with the window removed. As this variation was found to be the same in both cases, it was evident that the window introduced no appreciable error.

The measuring cell was made of a six-inch length of the same standard X-band wave guide as the rest of the system. It was silver plated on the inside, and enclosed in a water jacket for temperature control. The micrometer driving the plunger had a decimal thread with a pitch of 1 mm. and 50 divisions on the micrometer head giving positions accurately to 0.002 cm. After experimentation with three types of reflecting plunger, an open circuit plunger similar to one which has been previously described⁹ was adopted for most

(4) Roberts, *Electronics*, 19, No. 7, 130 (1946).

(5) Smyth and Walls, *THIS JOURNAL*, 54, 1854 (1932).

(6) Heston, Hennelly and Smyth, *ibid.*, 70, 4093 (1948).

(7) Manufactured for the U. S. Navy Department, Bureau of Ships, by Airadio Incorporated, Stamford, Conn.

(8) Manufactured for the U. S. Navy Department, Bureau of Ships, by the Hazeltine Electronics Corporation, New York, N. Y.

(9) Surber, Technical Report No. 1, ONR Contract N6ori-105, Task Order IV; *J. Applied Phys.*, 19, 514 (1948).

of the measurements because of its relative simplicity of construction, ruggedness, and assurance of steady plunger motion.

The temperature of the measuring cell from 25° to 55° was controlled by circulating water from five gallon constant temperature baths, held to within 0.1° by mercury-toluene regulators. The temperature of 1° was obtained by circulating water from a one gallon Dewar vessel filled with blocks of ice. The cell temperature was observed directly with an Anschütz thermometer placed in a thermometer well. The Anschütz thermometer had previously been calibrated against a National Bureau of Standards thermometer. For the 25° and 40° measurements the cell temperature never varied more than $\pm 0.1^\circ$ from the recorded value, while for the 1° and 55° measurements the fluctuations were as much as $\pm 0.2^\circ$. The dielectric measurements were always performed in the sequence, 25, 40, 55, 1° and a check measurement at 25° to make sure that the liquid had neither picked up any measurable amount of moisture nor appreciably attacked the cell or the plunger.

In the calculation of the 1.27 cm. results in the first paper⁶ of this series, a process of successive approximations was used in obtaining most of the results, as it was in the first part of the present work. The computational time can be reduced by a graphical method employing a set of curves for the dissipation factor,¹⁰ or by the following method, which was developed toward the end of the present work. The reflection coefficient of the dielectric sample in the cell, at positions of maximum or minimum reflected power, as observed on the output meter, is given by the following equation for the open circuit plunger

$$G_n^2 = \frac{G_\infty^2 \pm 2Fe^{-n\alpha\lambda_d/2} + e^{-n\alpha\lambda_d}}{1 \pm 2Fe^{-n\alpha\lambda_d/2} + G_\infty^2 e^{-n\alpha\lambda_d}} \quad (1)$$

where G_n is the reflection coefficient at the n^{th} position of maximum or minimum intensity, G_∞ is the reflection coefficient of an infinite column of dielectric, α is the attenuation constant of the dielectric material, λ_d is the wave length in the dielectric material, F is a function of ϵ' and ϵ'' , characteristic of the dielectric material. The plus refers to a maximum when n is odd, and the minus to a minimum when n is even. Since in this method the power measured is proportional to the square of the reflection coefficient but the proportionality factor, which depends upon the incident power, is not known, it is more convenient to work with ratios. The ratio M_n of the power at the n^{th} maximum or minimum position to that with the plunger at an effectively infinite distance from the window is used. This, however, requires the infinity value of the measured output, which, for some substances of lower than normal loss, could not be determined directly. The following extrapolation method was, therefore, used. Equation (1) for large n , reduces to

(10) Surber, Technical Report No. 2, ONR contract N6ori-105, Task Order IV.

$$M_n = \frac{G_n}{G_\infty} = 1 \pm \frac{2F}{G_\infty^2} e^{-n\alpha\lambda_d/2} \quad (2)$$

or, taking natural logarithms of both sides

$$\ln(M_n - 1) = \ln(2F/G_\infty^2) - n\alpha\lambda_d/2 \quad (3)$$

Therefore, provided G_∞^2 has its true value, $\ln(M_n - 1)$ plotted against n will give a straight line, on which values for both the maxima and the minima will lie. If not, then the maxima will be on one side and the minima on the other.

The extrapolation consists of choosing a value for the infinity output reading, and plotting the values of $\ln(M_n - 1)$ calculated from the experimental output readings at both maxima and minima against n . The value for the infinity reading giving the best straight line is chosen. In addition, this procedure enables one to estimate a value of the loss factor, ϵ'' , that may be substituted into the more exact equations to give the true value as the second approximation, since the slope of the plot of equation (3) is $-\alpha\lambda_d/2$ and

$$\epsilon'' = \alpha\lambda_0^2/\pi\lambda_d \quad (4)$$

where λ_0 is the wave length in free space.

From the spread of the values obtained from M , the values of ϵ'' are estimated as good to 2%. Since any set of measurements found to exhibit an uncertainty in λ_d of more than 0.5% was repeated, the error in the values of the dielectric constant, ϵ' , should be less than 1%. Quite independently of these considerations, one can check the precision or internal consistency of the measured dielectric constants and loss factors by plotting them against temperature for the various compounds. Smooth curves are to be expected for each compound and the plots representing successive members of an homologous series should show a gradual change from one substance to the next. This was found to be the case and, except for two or three points which were out of line by as much as 2%, the great majority of the ϵ' and ϵ'' values appeared to be self-consistent to within 0.5%.

The measurement frequency read from the frequency meter in the test set was always within the range of 9310 \pm 1 megacycles. No correction was made for varying room temperature or humidity since this correction is less than $\pm 0.007\%$ for the extremes encountered in the laboratory. The corresponding free space wave length is $\lambda_0 = 3.219 \pm 0.0005$ centimeters.

Experimental Results

The values of the dielectric constant, ϵ' , the loss factor, ϵ'' , and the loss tangent, ϵ''/ϵ' , measured for twenty-five liquid organic halides are given in Tables I, II and III. The results given for nonyl bromide, which is hard to purify, and tetradecyl bromide, which was used as furnished by the manufacturer, are to be considered as preliminary. A number of the measurements which were made a few tenths of a degree above or below the temperatures indicated were extrapolated or inter-

polated to these temperatures. Of these substances, *n*-octyl bromide, chlorobenzene, α -chloronaphthalene, ethylene chloride and ethylene bromide were measured by Mr. Alan D. Franklin. The liquids were purified, for the most part, by

TABLE I
DIELECTRIC CONSTANTS AT 3.22 CM.

	1.0°	25.0°	40.0°	55.0°
Ethyl bromide	9.50	8.87		
<i>n</i> -Propyl bromide	7.39	7.18	7.00	6.79
<i>i</i> -Propyl bromide	9.26	8.80	8.42	8.02
<i>n</i> -Butyl bromide	5.53	5.70	5.61	5.47
<i>i</i> -Butyl bromide	6.04	6.01	5.91	5.78
<i>s</i> -Butyl bromide	7.59	7.63	7.45	7.21
<i>t</i> -Butyl bromide	9.66	9.04	8.75	8.21
<i>n</i> -Amyl bromide	4.30	4.53	4.57	4.55
<i>n</i> -Hexyl bromide	3.75	4.03	4.14	4.15
<i>n</i> -Heptyl bromide	3.37	3.56	3.68	3.71
<i>n</i> -Octyl bromide	3.10	3.28	3.41	3.48
<i>n</i> -Nonyl bromide	2.84	3.05	3.17	3.16
<i>n</i> -Decyl bromide	2.71	2.88	2.97	3.05
<i>n</i> -Dodecyl bromide	2.58	2.68	2.74	2.83
<i>n</i> -Tetradecyl bromide	2.52	2.64	2.69	2.75
<i>n</i> -Hexadecyl bromide		2.52	2.57	2.62
<i>n</i> -Octyl chloride	3.22	3.50	3.61	3.63
<i>n</i> -Octyl iodide	2.78	2.97	3.03	3.07
Chlorobenzene	4.42	4.64	4.66	4.63
Bromobenzene	3.62	3.92	4.06	4.16
α -Chloronaphthalene	3.16	3.08	3.13	3.24
α -Bromonaphthalene	2.99	3.02	3.07	3.12
Ethylene chloride	8.91	9.01	8.62	8.24
Ethylene bromide		4.02	4.17	4.23
Tetramethylene chloride	6.56	7.09	7.30	7.28

TABLE II
LOSS FACTORS AT 3.22 CM.

	1.0°	25.0°	40.0°	55.0°
Ethyl bromide	2.14	1.54		
<i>n</i> -Propyl bromide	2.53	1.94	1.63	1.33
<i>i</i> -Propyl bromide	2.82	2.05	1.66	1.41
<i>n</i> -Butyl bromide	2.26	1.87	1.60	1.38
<i>i</i> -Butyl bromide	2.47	1.92	1.61	1.35
<i>s</i> -Butyl bromide	3.36	2.53	2.07	1.76
<i>t</i> -Butyl bromide	3.57	2.55	2.09	1.64
<i>n</i> -Amyl bromide	1.72	1.60	1.49	1.34
<i>n</i> -Hexyl bromide	1.37	1.38	1.34	1.21
<i>n</i> -Heptyl bromide	1.17	1.11	1.08	1.01
<i>n</i> -Octyl bromide	0.93	0.90	0.90	0.87
<i>n</i> -Nonyl bromide	.76	.82	.83	.76
<i>n</i> -Decyl bromide	.63	.71	.71	.69
<i>n</i> -Dodecyl bromide	.42	.51	.54	.54
<i>n</i> -Tetradecyl bromide	.37	.47	.49	.50
<i>n</i> -Hexadecyl bromide		.37	.40	.41
<i>n</i> -Octyl chloride	1.09	1.04	.96	.86
<i>n</i> -Octyl iodide	0.64	0.72	.72	.70
Chlorobenzene	1.66	1.41	1.21	1.01
Bromobenzene	1.36	1.34	1.26	1.12
α -Chloronaphthalene	0.49	0.63	0.70	0.76
α -Bromonaphthalene	0.36	0.51	0.59	0.66
Ethylene chloride	3.97	2.79	2.18	1.77
Ethylene bromide		0.95	0.89	0.77
Tetramethylene chloride	3.42	2.86	2.45	2.00

TABLE III
LOSS TANGENTS AT 3.22 CM.

	1.0°	25.0°	40.0°	55.0°
Ethyl bromide	0.225	0.174		
<i>n</i> -Propyl bromide	.342	.270	0.233	0.196
<i>i</i> -Propyl bromide	.305	.233	.197	.176
<i>n</i> -Butyl bromide	.408	.328	.285	.252
<i>i</i> -Butyl bromide	.409	.320	.273	.234
<i>s</i> -Butyl bromide	.443	.332	.278	.244
<i>t</i> -Butyl bromide	.369	.282	.239	.200
<i>n</i> -Amyl bromide	.400	.353	.326	.295
<i>n</i> -Hexyl bromide	.365	.342	.324	.292
<i>n</i> -Heptyl bromide	.347	.312	.294	.272
<i>n</i> -Octyl bromide	.300	.276	.264	.250
<i>n</i> -Nonyl bromide	.268	.269	.259	.241
<i>n</i> -Decyl bromide	.232	.247	.239	.226
<i>n</i> -Dodecyl bromide	.159	.190	.197	.187
<i>n</i> -Tetradecyl bromide	.147	.178	.182	.182
<i>n</i> -Hexadecyl bromide		.143	.156	.157
<i>n</i> -Octyl chloride	.339	.297	.266	.237
<i>n</i> -Octyl iodide	.229	.243	.238	.227
Chlorobenzene	.374	.305	.261	.219
Bromobenzene	.376	.342	.310	.269
α -Chloronaphthalene	.155	.204	.223	.233
α -Bromonaphthalene	.117	.169	.192	.212
Ethylene chloride	.444	.309	.255	.215
Ethylene bromide		.236	.214	.182
Tetramethylene chloride	.522	.403	.336	.275

Mr. William M. Heston, Jr. The methods of purification and the criteria of purity will be described in another paper.

Discussion of Results

The results will be used in a subsequent paper with those obtained⁶ at 1.27 cm. to analyze the molecular behavior in the liquids, but certain aspects of the measurements may be profitably examined here. A more generally exact representation¹¹ of the dielectric constant, ϵ' , than that given by the Debye equations³ is given by the equation

$$\epsilon' - \epsilon_{\infty} = \frac{\epsilon_0 - \epsilon_{\infty}}{2} \left[1 - \frac{\sinh(1 - \alpha)x}{\cosh(1 - \alpha)x + \sin(\alpha\pi/2)} \right] \quad (5)$$

in which ϵ_{∞} is the dielectric constant at infinite frequency, ϵ_0 the static dielectric constant, $x = \ln(\omega\tau_0)$ where ω , the angular frequency, is 2π times the frequency in cycles/sec. and τ_0 is the most probable relaxation time, and α is an empirical distribution constant, not to be confused with the previously used attenuation factor. This differs from the original Cole and Cole equation in having $\sin(\alpha\pi/2)$ in the denominator instead of $\cos(\alpha\pi/2)$, which appears to be incorrect. The Cole and Cole expression for the loss factor is

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_{\infty})\cos(\alpha\pi/2)}{2[\cosh(1 - \alpha)x + \sin(\alpha\pi/2)]} \quad (6)$$

Cole and Cole¹¹ have shown that when the values of ϵ'' at different frequencies are plotted as ordinates against the corresponding values of ϵ' as

(11) Cole and Cole, *J. Chem. Phys.*, **9**, 341 (1941).

abscissas, the arc of a circle is obtained. The points at which ϵ' has the values ϵ_∞ and ϵ_0 are the points of intersection with the abscissa axis. When α is zero, that is, when there is only one relaxation time, the arc is a semicircle with its diameter in the abscissa axis. When there is a distribution of relaxation times, the center of the semicircle is depressed, as shown in Fig. 1, through an angle $\alpha' = \alpha\pi/2$, which is a measure of the extent of the distribution. The value of α may be calculated from the angles α' , β and γ in Fig. 1, since it may easily be shown that

$$\tan \beta = (\epsilon_0 - \epsilon')/\epsilon'' \quad (7)$$

$$\tan \gamma = (\epsilon' - \epsilon_\infty)/\epsilon'', \text{ and} \quad (8)$$

$$\alpha' = \beta + \gamma - \pi/2 \quad (9)$$

The values of the static dielectric constant, ϵ_0 , measured by Mr. W. M. Heston at 520 kc., will be given in another paper. For ϵ_∞ , the square of the refractive index for the D sodium line, n^2_D , has been used in the present work. It will be shown in a subsequent paper that a more consistent representation of the data observed at different wave lengths is obtained by using a slightly higher value of ϵ_∞ containing a calculated contribution from atomic polarization. The values of α' and hence α have been calculated by means of equations (7), (8) and (9) and substituted in equation (6) along with those of ϵ_0 , ϵ_∞ and ϵ'' to calculate τ_0 , from which the critical wave length, λ_m , at which the loss factor is a maximum, has also been calculated by means of the relation, $\lambda_m = 2\pi c\tau_0$, where c is the velocity of light.

The values obtained for α and τ_0 from the 3.22 cm. measurements have been substituted in equations (5) and (6) and used to calculate values of ϵ' and ϵ'' at 9.72 cm. The calculated ϵ' values for eleven substances agree as well with those observed¹² at 9.72 cm. as do the ϵ' values observed by measuring wave minima with those obtained from wave maxima at 9.72 cm. The calculated loss factor values are consistently 10 to 15% lower than the values observed at 9.72 cm., which are believed to be high by nearly that amount.

The values of α calculated from the 3.22 cm. measurements tend to be somewhat lower than those calculated from the 1.27 cm. values by means of equations (7), (8) and (9) and the values of λ_m are generally slightly higher. They are not reproduced here, because the use of the slightly higher value of ϵ_∞ obtained by taking account of the atomic polarization will give better agreement and the use of the Cole and Cole plot with this higher value will combine the two sets of measurements to give more satisfactory values of α and λ_m . It may be concluded, however, that the distribution of relaxation times, as measured by α , increases with increasing length of the molecule and decreases with rising temperature and that the critical wave length increases with increasing chain length and is still increasing when the 16-carbon chain has been reached.

(12) Schneider, Magat and Laquer, unpublished measurements.

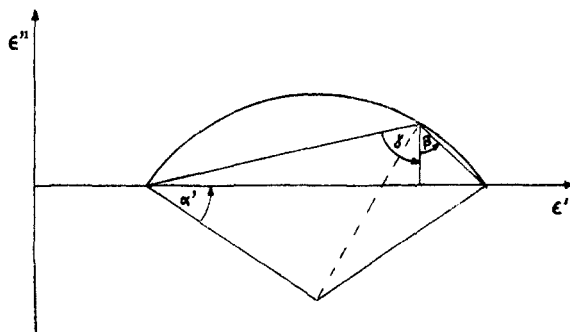


Fig. 1.—The Cole and Cole arc plot.

The calculation of τ_0 which has been employed involves the assumption that a factor, $(\epsilon_0 + 2)/(\epsilon_\infty + 2)$, in the Debye equation³ may be neglected in conformity with the Onsager treatment¹³ of the internal field. If the Debye treatment⁸ is used, the calculated relaxation time is altered by a factor $(\epsilon_\infty + 2)/(\epsilon_0 + 2)$. The relaxation times have been used to calculate the thermodynamic quantities governing the relaxation process according to the methods of absolute rate theory.^{2,14,15} The values of τ_0 , which are calculated without the previously mentioned factor, give slightly higher values of ΔF^\ddagger , the free energy of activation for the dipole relaxation process, and ΔH^\ddagger , the heat of activation, and much the same values of ΔS^\ddagger , the entropy of activation. The differences are too small to affect any conclusions to be drawn and certainly far too small to throw any light upon the problem of the internal field. As it is hoped that more accurate values will be obtained for these quantities in subsequent work, the numerical values and curves for the quantities are omitted from the present paper. The values of ΔF^\ddagger increase with increasing molecular size from about 1.6 kcal./mole for ethyl bromide to about 3.5 for hexadecyl bromide, those of ΔH^\ddagger from about 1 for ethyl bromide to about 4 for hexadecyl, and those of ΔS^\ddagger from about -3 entropy units per mole to about +4. The same quantities for the process of viscous flow were calculated¹⁴ from the viscosities measured by Mr. Edward J. Hennelly in this Laboratory.

As previously observed² for other liquids, the free energies and heats of activation for dielectric relaxation are lower than those for viscous flow, which involves translational motion of the molecules in addition to the rotational motion required in both processes. The close parallelism in the trends of the two sets of values indicates the similarity of the two processes. While the entropy of activation for viscous flow is negative for all these alkyl bromides, it becomes less negative with increasing size of the larger molecules, paralleling the change from negative to positive values in the di-

(13) Onsager, *THIS JOURNAL*, **58**, 1486 (1936).

(14) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, New York, N. Y., 1941, Chap. IX.

(15) Kauzmann, *Revs. Modern Phys.*, **14**, 12 (1942).

electric relaxation process. It would appear that an increased degree of orientation of the longer molecules in the liquid with increased molecular length necessitates a greater decrease in order in the system to attain the activated state. In other words, the trend of the entropies indicates an increasingly ordered liquid structure as the molecular chain length increases.

Summary

An apparatus for the measurement at a wave length of 3.22 cm. of the dielectric constants and loss factors of high loss liquids is briefly described and certain aspects of the method are discussed.

The dielectric constants, loss factors and loss tangents at temperatures from 1° to 55° are given for ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *s*-butyl, *t*-butyl, *n*-amyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-nonyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl and *n*-hexadecyl bromides, and *n*-octyl chloride, *n*-octyl iodide, chlorobenzene, bromobenzene, α -chloro-

naphthalene, α -bromonaphthalene, ethylene chloride, ethylene bromide and tetramethylene chloride.

The dielectric relaxation times and their distribution parameters are calculated and the temperature dependence of the former is used to calculate the free energies, heats and entropies of activation for the molecules. The actual values of these quantities will be given in the third paper of this series, but it is found that the distribution of relaxation times increases with increasing length of the molecule and decreases with rising temperature. A close similarity is observed between the behavior of these thermodynamic quantities for the process of dielectric relaxation and that of the same quantities for viscous flow. The increase observed in the entropy of activation with increasing molecular length is regarded as evidence of increasingly ordered orientation of the molecules in the liquid structure.

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Microwave Absorption and Molecular Structure in Liquids. III. Dielectric Relaxation and Structure in Organic Halides¹

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The Debye theory of dielectric absorption provided equations capable of approximate representation of the experimentally observed phenomena and a mechanism in terms of which the molecular behavior during absorption could be roughly pictured. The picture of a dielectric material as consisting of spherical molecules whose rotation in an externally applied alternating electric field obeys Stokes' law is obviously a rough approximation in most cases. The fundamental quantity involved in this treatment is the relaxation time, the time required after the removal of an externally applied field for the polarization of the material to fall to $1/e$ of its initial value. Analysis has shown that the observed dielectric behavior can commonly be well represented by a distribution of relaxation times with a maximum probability of occurrence at a frequency corresponding to the critical frequency at which the dielectric loss, ϵ'' , has a maximum value. Much of the work on dielectric loss has been empirical and the introduction of a distribution of relaxation times has given added adjustable parameters, the values of which are obtained empirically and are incapable of yielding much information about mechanism unless they are considered as part of a body of informations about materials with clearly defined structures. The first two papers^{2,3} of this series have provided

data on the dielectric constants and loss factors of twenty-seven liquids which will be used in the present paper in an examination of the theory and mechanism of dielectric absorption.

Dependence of Dielectric Constant and Loss Factor upon Frequency

The Debye equations⁴ for the dependence of dielectric constant and loss factor upon frequency are

$$\epsilon' = \epsilon_{\infty} + (\epsilon_0 - \epsilon_{\infty})/(1 + x^2) \quad (1)$$

and

$$\epsilon'' = (\epsilon_0 - \epsilon_{\infty})x/(1 + x^2) \quad (2)$$

where ϵ' = dielectric constant measured at frequency, f ; ϵ'' = loss factor; ϵ_0 = dielectric constant at zero frequency; ϵ_{∞} = dielectric constant at infinite frequency; and

$$x = B\omega\tau \quad (3)$$

where

$$B = (\epsilon_0 + 2)/(\epsilon_{\infty} + 2) \quad (4)$$

ω = angular frequency = $2\pi f$; and τ = the relaxation time. Equation (1) requires that ϵ' decrease from ϵ_0 to ϵ_{∞} with increasing frequency, most of the decrease occurring within a hundred-fold frequency range or within two logarithmic units of frequency or wave length as shown by the solid line A in Fig. 1. In this same range, equation (2) requires that ϵ'' change from a small value

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(2) Heston, Hennelly and Smyth, *THIS JOURNAL*, **70**, 4093 (1948).

(3) Laquer and Smyth, *ibid.*, **70**, 4097 (1948).

(4) Debye, "Polar Molecules," *The Chemical Catalog Co.*, New York, N. Y., 1929, Chap. V.