Summary

Solubility parameters (square roots of the internal pressure) have been calculated for fluorocarbons, and are lower than any other substances liquid at room temperature. From the Hildebrand solubility theory we deduce that the aliphatic fluorocarbons are completely miscible with aliphatic hydrocarbons and ether, but show only limited solubility in benzene, acetone, etc. Experimental data confirm these predictions, leading to the conclusion that the solubilities of the fluorocarbons are not at all anomalous but are only the thermodynamic consequences of their low solubility parameters.

LOS ANGELES, CALIFORNIA RECEIVED JULY 20, 1948

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. I. Measurement in Organic Halides at 1.27 Cm. Wave Length[1]

BY WILLIAM M. HESTON, JR., EDWARD J. HENNELLY AND CHARLES P. SMYTH

Dielectric constant and loss factor measurements at a wave length of 9.72 cm. carried out in this Laboratory on water[2] and preliminary measurements upon some twenty organic liquids,[2,3] as well as many measurements scattered through the literature, made evident the desirability of employing newly developed apparatus and techniques in a systematic study of dielectric loss and its dependence upon molecular structure. Such measurements have been made upon the alkyl bromides, the molecules of which vary from the short, compact structures of ethyl bromide and the branched-chain propyl and butyl bromides to the long, flexible and possibly coiled structures of *n*-tetradecyl and *n*-hexadecyl bromides. Rigid molecules, such as those of bromobenzene, chlorobenzene, α-bromonaphthalene, and α-chloronaphthalene have also been measured for comparison.

The present paper describes the method and apparatus devised for the measurement at a wave length of 1.27 cm. and reports the values of the dielectric constants and loss factors obtained for 27 pure liquids at temperatures of 1, 25, 40 and 55°. The purification of the liquids, the values of other physical constants necessary for the interpretation of the results and the application of dielectric theory to the results will be given in subsequent papers, which will include other measurements in the 1 to 30 cm. wave length region.

Experimental Method and Apparatus

This method,[4] which was developed in collaboration with Mr. W. H. Surber, Jr.,[5] is especially suited to the measurement of liquids which have high dielectric loss at the frequency employed. It is based upon the variation in the reflection coefficient of a uniform dielectric layer as the depth of the layer is varied. The termination of the dielectric layer may be either a short-circuit, or a high impedance circuit. The results contained in this report were obtained with apparatus using a highly conducting termination (short-circuit). Since a directional coupler is used to measure directly the reflected power, the calculations involve only the ratio of the amplitudes of the reflected wave for two different lengths of the dielectric-filled guide. In addition, the wave lengths in the dielectric-filled guide and the air-filled guide are required. Thus, measurement of the shift in the minimum point, such as is required in impedance methods, is eliminated. Since the liquids measured exhibit high loss at this frequency, the waveguide equations are carried through without approximation.

A functional diagram of the apparatus used to measure dielectric constant and absorption is shown in Fig. 1. The 2K33 Raytheon klystron oscillator is square-wave modulated at 1000 c.p.s., since sine wave modulation produces some disturbing frequency modulation. A calibrated resonant cavity wavemeter is used to measure the output wave length, λ_0, of the oscillator, while the wave length in the air-filled guide, λ_g, is measured with the slotted line. The cut-off wave length of the air-filled guide can be easily calculated from these values. An

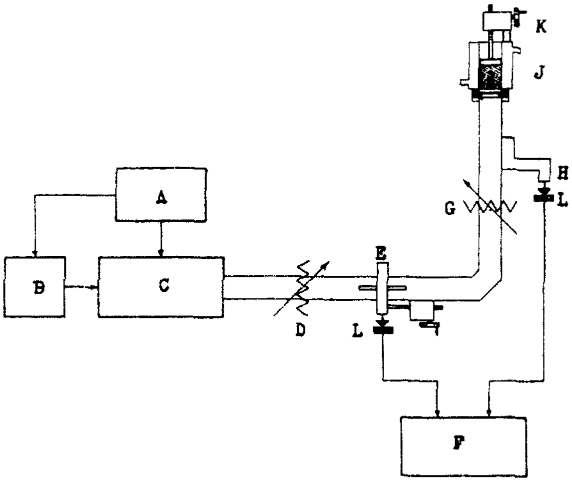

Fig. 1.—Apparatus for measurement at 1.27 cm.: (A) regulated power supply, (B) modulator, (C) 2K33 oscillator, (D) decoupling attenuator, (E) traveling detector, (F) audio amplifier, (G) matching attenuator, (H) directional coupler, (J) thermostated cell, (K) micrometer drive mechanism, (L) 1N26 crystal detectors.

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[1] This research was carried out with the support of the Office of Naval Research.

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

[3] Magat, Schneider and Smyth, unpublished measurements.

[4] Heston, Hennelly and Smyth, Report No. 10, ONR Contract N6ori-105, Task Order IV.

[5] Surber, Technical Report No. 1, ONR Contract N6ori-105, Task Order IV; *J. Applied Phys.*, **19**, 514 (1948); Crouch, *J. Chem. Phys.*, **16**, 364 (1948).

electronically regulated power supply insures stability of operating voltages supplied to the 2K33 oscillator.

Determination of the 1N26 crystal characteristics in the power region used is necessary. In the writers' laboratory the crystals are calibrated and their response characteristics determined in one simple operation[6] using the slotted line and its micrometer unit. In the power range used the exponent of the crystal response was found to be 2.00 ± 0.02. The crystal, thus, is acting as a square-law detector over the entire range covered in the experiments.

A variable resistance strip attenuator is used to decouple the 2K33 oscillator from the system to prevent "pulling," or frequency variation due to changes in loading. In practice the oscillator output frequency has been found to be remarkably constant.

A second variable attenuator which is matched looking toward the dielectric cell is placed immediately before the directional coupler. (The attenuator must be matched so that it does not reflect energy.) Its presence is necessitated by the use of the right-angle bend which permits vertical positioning of the dielectric cell, eliminating the problem of liquid-tight plunger seals. In general, there will be some reflection of energy from the right-angle bend, which would effectively vary the incident power as the depth of the dielectric layer is varied. This reflection of energy from the right-angle bend must be attenuated to insure a constant incident power, an assumption upon which the calculations are based.

The highly selective, variable tuned audio amplifier, Model TAA-16EA, receives and amplifies the detected modulation frequency. The amplifier has been found to be linear over the entire operating range. The directional coupler has a coupling coefficient of 23 db. and a directivity of 35 db. Thus, it greatly attenuates incident power from the oscillator, but permits passage of reflected energy from the dielectric-filled cell to the audio amplifier.

A mica window 0.0076 cm. thick serves to separate the liquid dielectric from the remainder of the waveguide system. For a matched load placed in the dielectric cell the voltage standing wave ratio, VSWR, was found to be approximately 1.2. This mica window, if not matched out, would serve as an impedance transformer, thereby preventing direct observation of the reflection coefficient of the liquid dielectric layer. A number of methods will accomplish matching out of the window; in this system, however, a metallic inductive window has been placed immediately before the mica window. With proper adjustment of the matching attenuator and insertion of the inductive matching window the VSWR was 1.04 ± 0.01.

The dielectric cell is a four-inch section of coin silver waveguide jacketed to permit thermostating. The plunger is made of brass and is an adaptation of the non-contact type commonly employed in air-filled wave guides. This type is constructed so that its face appears as a short circuit to the incident wave, irrespective of discrepancies in the contact resistance between the back of the plunger and the waveguide. An air-type plunger, however, cannot be used in a liquid dielectric-filled waveguide system, for with different liquids the quarter wave lengths are not of equal length, and thus an effective short is not obtained when the same plunger is used for all liquids. However, a plunger (Fig. 2) has been constructed with teflon to fill the slots and thus present an effective short at 1.27 cm. The teflon prevents liquid from entering the slots, and is resistant to organic liquids. From the dielectric constant of teflon ($\epsilon' = 2.06$ at 1.25 cm.) the half wave length may be calculated by means of equation (3) since ϵ'' is very small at 1.25 cm. The length in teflon from the face of the plunger to the end of the slot is 0.492 cm. or one-half wave length. The distance between the elbow in the teflon and the back end of the teflon slab is not critical. Two thin grooves are cut along the narrow sides of the plunger to permit passage of the liquid as the plunger is moved.

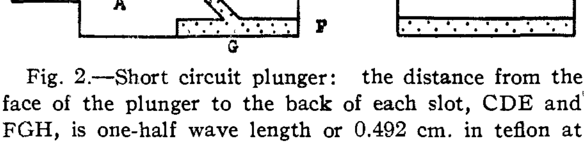

Fig. 2.—Short circuit plunger: the distance from the face of the plunger to the back of each slot, CDE and FGH, is one-half wave length or 0.492 cm. in teflon at 1.25 cm.; (A) brass, (B) teflon.

A micrometer drive mechanism, Radiation Laboratory Type 1557, is used to vary the depth of the dielectric layer by moving the plunger. The micrometer unit and dielectric cell are mounted as a single unit to ensure reproducible positioning of the cell and micrometer. The position of the plunger and, thus, the depth of the dielectric layer can be read to 0.0002 cm. This amounts to an error of 0.2% or less in determining the wave length, λ_d, in the dielectric medium.

Analysis of Experimental Method

The wave length in an air-filled wave guide for any mode is

$$\lambda_g = \lambda_0/(1 - (\lambda_0/\lambda_c)^2)^{1/2} \qquad (1)$$

where λ_0 is the free space wave length, and λ_c is the cutoff wave length of the wave guide.[7] The K-band wave guide used in this equipment is so designed as to permit only the TE_{10} mode. A resonant cavity wavemeter was used to measure λ_0, and λ_g was measured by means of a slotted line, Model TPK-21 HU, identical in dimensions with the waveguide used in the cell. λ_c was then evaluated by writing equation (1) in the form

$$\lambda_c = \lambda_g\lambda_0/(\lambda_g^2 - \lambda_0^2)^{1/2} \qquad (2)$$

Once the values of λ_g and λ_0 are obtained they remain as constants, provided the frequency of the 2K33 oscillator does not drift. The effect upon λ_c of the temperature changes used in these measurements is negligibly small.

The complex dielectric constant ϵ^* may be written as $\epsilon^* = \epsilon' - j\epsilon''$, where ϵ' is the real part, and ϵ'' is the loss factor. Where the effect of the loss factor is negligible, the dielectric constant ϵ^* is equal to ϵ'.

$$\epsilon^* = \epsilon' = (\lambda_0/\lambda_d)^2 + (\lambda_0/\lambda_c)^2 \qquad (3)$$

Thus, for very low loss dielectrics, the dielectric constant may be found by merely measuring the wave length, λ_d, in the dielectric medium. The value of λ_d is twice the distance between successive minima as observed on the micrometer drive mechanism. For a dielectric which has a high loss, however, the exact wave guide equations must be employed

$$\epsilon' = (\lambda_0/\lambda_d)^2 + (\lambda_0/\lambda_c)^2 - (\epsilon''\lambda_d/2\lambda_0)^2 \qquad (4)$$

It must be pointed out that λ_d is affected by the loss factor. This can be shown by writing the expression for λ_d in the form

$$\lambda_d = 2^{1/2}\lambda_0/(\epsilon' - (\lambda_0/\lambda_c)^2)^{1/2}(1 + (D^2 + 1)^{1/2})^{1/2} \qquad (5)$$

where D the dissipation factor is

$$D = \epsilon''/(\epsilon' - (\lambda_0/\lambda_c)^2) \qquad (6)$$

The evaluation of ϵ'' is obtained by measuring the variation in the reflected power as the depth

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[6] Krutter, Radiation Laboratory Report, R. L. 54.10.

[7] Microwave Techniques, Navships, 900.028 (1944).

of the dielectric layer is increased. The position of the plunger and meter readings at each maximum and minimum are recorded. The depth of the dielectric layer is increased until any further increase produces no variation in the reflection coefficient. This is essentially equivalent to an infinite dielectric layer, and, for the high and medium loss halides reported in this paper, occurs within five or six minima, at the most. Thus, from the ratio of any one maximum meter reading to that for the infinity value and from the measured λ_d, both ϵ' and ϵ'' may be calculated. The evaluation of ϵ'', however, involves the process of successive approximation.

An electromagnetic wave propagated through a a distance x in a waveguide can be represented by

$$E = E_0 e^{-\gamma x} \tag{7}$$

where γ is the propagation constant. For a dielectric-filled waveguide γ can be written as

$$\gamma = 2\pi((\lambda_0/\lambda_c)^2 - \epsilon' + j\epsilon'')^{1/2}/\lambda_0 = \alpha + j\beta \tag{8}$$

where α is the attenuation constant and β is the phase constant. Writing this expression in rectangular form

$$\alpha = \pi\epsilon''/\lambda_0((1/2 + (1 + D^2)^{1/2}/2)^{1/2}(\epsilon' - (\lambda_0/\lambda_c)^2)^{1/2} \tag{9}$$

$$\beta = 2\pi(1/2 + (1 + D^2)^{1/2}/2)(\epsilon' - (\lambda_0/\lambda_c)^2)^{1/2}/\lambda_0 \tag{10}$$

Combination of equations (5) and (9) yields

$$\alpha = \pi\epsilon''\lambda_d/\lambda_0^2 \tag{11}$$

In the actual computations the value of $\alpha\lambda_d$ is found and from it ϵ'' is calculated. In earlier work the value of ϵ'' was determined by the process of successive approximation. Table I indicates that an assumption of ϵ'' within 5% of the calculated value is satisfactory. The computational time can be greatly reduced, however, by using a graphical method employing a set of curves plotted for D, the dissipation factor.[8] Briefly, this procedure requires the conversion of the ratios of the reflection coefficients to ratios of the standing wave ratio (SWR). The infinity SWR is determined primarily by λ_d, which is measured, but it is also affected by the value of D for the high and medium loss dielectrics. Therefore, two graphs are used to estimate D. After an estimate of D is made and the graphs are employed to evaluate D, ϵ'' is easily calculated as in the previously used method of successive approximation.[4] Thus only one calculation of ϵ'' is required when D is determined graphically. For a complete explanation of both procedures, see references (4) and (8).

TABLE I

EFFECT OF APPROXIMATION UPON CALCULATED VALUE OF ϵ'' FOR *s*-BUTYL BROMIDE

Assumed ϵ''	Calculated ϵ''
1.50	3.44
3.40	3.28
3.30	3.28

Experimental Procedure and Calculation

The actual experimental procedure and the calculation of the results are as follows: 5 ml. of the purified sample is placed in the thermostated dielectric cell and permitted to reach constant temperature. The plunger is lowered into the cell, adjusted so that it is at the first minimum adjacent to the mica window, and is then slowly withdrawn from the neighborhood of the mica window by means of a micrometer drive mechanism. At each minimum the position of the plunger and the output meter reading are recorded. At each maximum the output meter reading is recorded. The plunger is withdrawn until further withdrawal produces no appreciable variation in the output meter reading. This value is recorded as the infinity value. For the lower loss dielectrics the reflecting plunger must be withdrawn farther than for the higher loss dielectrics. Since the length of the cell is about 10 cm., it is sometimes necessary to insert a matched load which will give the infinity value directly. From the positions of the plunger at the minima, the wave length λ_d may be obtained. λ_d is equivalent to twice the distance between successive minima. From the maximum value of the output meter reading and the infinity value, the ratio, M, of the maximum peak value of the meter reading to the infinity value of the meter reading can be obtained. With λ_d and M experimentally determined, a value of D is estimated and the infinity SWR is obtained by entering the first graph at the value of λ_d on the curve of the estimated value of D. The infinity *SWR* so obtained is then used with M to calculate the ratio of the *SWR* at the maximum to the infinity *SWR*. This calculated ratio is then entered on the second graph and the value of D is obtained. Use of D yields $\alpha\lambda_d$, and ϵ'' is then determined by means of equation (11). The corrected value of ϵ' is then obtained by means of equation (4).

In the development of the mathematical theory, it was pointed out that successive maxima may be used to calculate the dielectric absorption. For the very high loss dielectrics, the first and second maxima have been used because rapid damping out of the reflected energy permits observation of only two or three maxima before the infinity value is reached. In the lower loss dielectrics the third, fourth, and often the fifth maxima are used to calculate the absorption. Values calculated from the ratios obtained for the first and second maxima for *i*-propyl bromide and *i*-butyl bromide are given in Table II.

TABLE II

CALCULATION OF ϵ' AND ϵ'' FROM SUCCESSIVE MAXIMA

	First maximum		Second maximum	
t, °C.	ϵ'	ϵ''	ϵ'	ϵ''
	i-Propyl Bromide			
1.0	6.45	4.06	6.44	4.09
25.0	6.78	3.47	6.76	3.57
40.0	6.82	3.03	6.80	3.13
55.0	6.79	2.66	6.78	2.72
	i-Butyl Bromide			
1.0	4.00	2.37	4.00	2.42
25.0	4.32	2.30	4.31	2.33
40.0	4.33	2.18	4.33	2.18
55.0	4.42	2.04	4.38	2.12

The values for the loss factor obtained from the first and second minima for *i*-propyl bromide agree within 3%, whereas the dielectric constants agree within 0.2%. In general the agreement is within the experimental error of the measurements.

Inspection of Table II will reveal that the loss factor obtained from the second maximum is somewhat larger than that obtained from the first. This trend can be explained on the basis of loss at the mica window and the inductive diaphragm. By using this inductive matching section at the mica window the loss due to power conversion to higher modes is greatly reduced. The higher modes set up are

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

attenuated without absorbing power in the dielectric before they reach the dielectric medium, since the matching section presents effectively a wave guide below cutoff to these higher modes.

Experimental Results

The values of the dielectric constant, ϵ', and the loss factor, ϵ'', are given in Tables III and IV. In Fig. 3 the loss tangents, ϵ''/ϵ', for the straight-chain alkyl bromides at 1° and at 55° are plotted against the number of carbon atoms in the chain. The similar curves at 25° and 40° are omitted in order to avoid complication of the diagram.

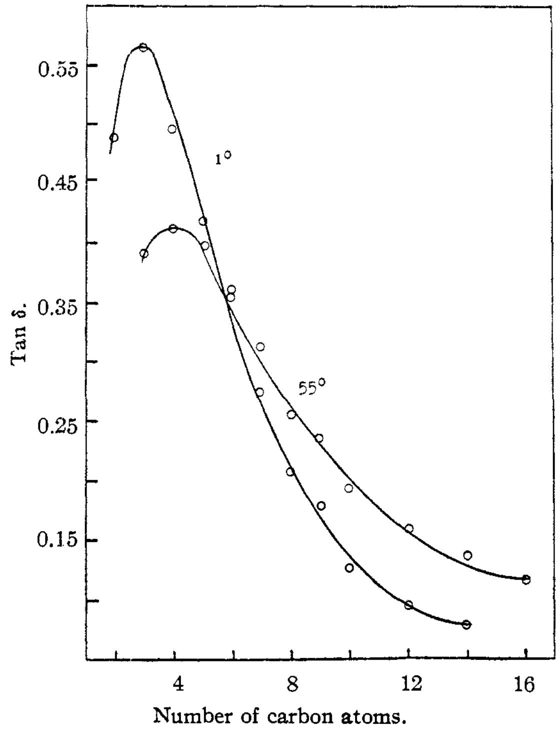

Fig. 3.—Dependence of the loss tangent upon chain length.

Discussion of Results

The observed values of the loss tangent lie satisfactorily close to the smooth curves in Fig. 3. The maximum on each of the two curves must be close to the maximum loss tangent which can be attained by the substance at that point; that is, the wave length, λ_t, at which the loss tangent has a maximum value, is approximately 1.27 cm. for *n*-propyl bromide at 1° and for *n*-butyl bromide at 55°. It can easily be shown from the equations of Debye[9] that the critical wave length, λ_m, at which ϵ'' reaches its maximum value, is given by the equation

$$\lambda_m = (\epsilon_0/\epsilon_\infty)^{1/2}\lambda_t \qquad (12)$$

in which ϵ_0 is the static dielectric constant and ϵ_∞, the dielectric constant at infinite frequency. Substitution for ϵ_0 and ϵ_∞ of values to be reported

Table III

Dielectric Constants at 1.27 Cm.

	1.0°	25.0°	40.0°	55.0°
Ethyl bromide	7.09	7.29	..	..
n-Propyl bromide	5.07	5.46	5.52	5.52
i-Propyl bromide	6.45	6.77	6.81	6.78
n-Butyl bromide	4.02	4.10	4.20	4.29
i-Butyl bromide	4.00	4.31	4.33	4.40
s-Butyl bromide	4.83	5.27	5.39	5.49
t-Butyl bromide	5.92	6.52	6.76	6.60
n-Amyl bromide	3.30	3.47	3.47	3.59
n-Hexyl bromide	2.96	3.11	3.18	3.26
n-Heptyl bromide	2.78	2.89	2.99	3.03
n-Octyl bromide	2.74	2.79	2.81	2.92
n-Nonyl bromide	2.57	2.66	2.73	2.77
n-Decyl bromide	2.50	2.59	2.59	2.63
n-Dodecyl bromide	2.40	2.43	2.45	2.49
n-Tetradecyl bromide	2.37	2.40	2.40	2.42
n-Hexadecyl bromide	..	2.35	2.38	2.39
n-Octyl chloride	2.76	2.89	2.95	3.01
n-Octyl iodide	2.54	2.59	2.62	2.65
n-Dodecyl chloride	2.45	2.50	2.55	2.58
Cyclohexyl bromide	3.22	3.33	3.52	3.56
Chlorobenzene	3.29	3.44	3.55	3.63
Bromobenzene	2.95	3.08	3.08	3.18
α-Chloronaphthalene	2.83	2.80	2.80	2.83
α-Bromonaphthalene	..	2.89	2.87	2.87
Ethylene chloride	5.64	6.14	6.49	6.67
Ethylene bromide	..	3.28	3.37	3.47
Tetramethylene chloride	4.42	4.79	5.08	5.36

Table IV

Loss Factors at 1.27 Cm.

	1.0°	25.0°	40.0°	55.0°
Ethyl bromide	3.46	2.70	..	..
n-Propyl bromide	2.86	2.53	2.36	2.18
i-Propyl bromide	4.08	3.53	3.08	2.70
n-Butyl bromide	2.00	1.97	1.84	1.77
i-Butyl bromide	2.40	2.32	2.18	2.08
s-Butyl bromide	3.39	3.28	3.03	2.75
t-Butyl bromide	4.29	3.95	3.52	3.14
n-Amyl bromide	1.39	1.45	1.39	1.43
n-Hexyl bromide	1.07	1.15	1.17	1.17
n-Heptyl bromide	0.77	0.87	0.91	0.95
n-Octyl bromide	.57	.69	.73	.75
n-Nonyl bromide	.46	.57	.63	.66
n-Decyl bromide	.32	.42	.47	.51
n-Dodecyl bromide	.23	.31	.36	.40
n-Tetradecyl bromide	.19	.26	.30	.33
n-Hexadecyl bromide	..	.21	.25	.28
n-Octyl chloride	.74	.86	.87	.88
n-Octyl iodide	.35	.44	.49	.52
n-Dodecyl chloride	.32	.41	.45	.49
Cyclohexyl bromide	1.36	1.66	1.78	1.83
Chlorobenzene	1.27	1.35	1.39	1.33
Bromobenzene	0.82	0.94	0.94	1.05
α-Chloronaphthalene	.19	.28	.33	0.37
α-Bromonaphthalene	..	.21	.25	0.31
Ethylene chloride	3.93	3.70	3.35	2.96
Ethylene bromide	..	0.80	0.86	0.89
Tetramethylene chloride	2.48	2.73	2.80	2.80

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

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 theory[9]

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

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 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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[10] Onsager, THIS JOURNAL, 58, 1486 (1936).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. II. Measurement in Organic Halides at 3.22 Cm. Wave Length[1]

BY HENRY L. LAQUER[1a] AND CHARLES P. SMYTH

Preliminary measurements of the dielectric constants and loss factors at 9.72 cm. wave length of a considerable number of organic molecules[2] 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. apparatus[2] 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

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[1] This research was partially supported by the Office of Naval Research.

[1a] Present address: Los Alamos Scientific Laboratory, Los Alamos, N. M.

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

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