The fraction of excited molecules that reacts with hydroxide ion at the time of excitation is

$$K(\mathrm{OH}^-)/(1 + K(\mathrm{OH}^-)) \qquad (1)$$

the fraction that does not is

$$1/(1 + K(\mathrm{OH}^-)) \qquad (2)$$

Of this last fraction the fraction

$$1/(1 + k_q(\mathrm{OH}^-)) \qquad (3)$$

emits the fluorescence of the neutral excited α-naphthylamine molecule and the fraction

$$k_q(\mathrm{OH}^-)/(1 + k\ (\mathrm{OH}^-)) \qquad (4)$$

reacts with hydroxide ion; $k_q = k_2/k_1$.

The molecules that react with hydroxide ion fluoresce with the apparent efficiency c_2.

In the solution containing hydroxide ion the intensity of fluorescence from neutral excited α-naphthylamine molecules is the product of *2*, *3* and I_0

$$I_0\left[\frac{1}{1 + K(\mathrm{OH}^-)}\right] + \left[\frac{1}{1 + k_q(\mathrm{OH}^-)}\right] \qquad (5)$$

The measured intensity of fluorescence from the molecules that react with hydroxide ion is the product of c_2, *1* and I_0 plus the product of c_2, *2*, *4* and I_0

$$I_0c_2\left\{\left[\frac{K(\mathrm{OH}^-)}{1 + K(\mathrm{OH}^-)}\right] + \left[\frac{1}{1 + K(\mathrm{OH}^-)}\right]\left[\frac{k\ (\mathrm{OH}^-)}{1 + k_q(\mathrm{OH}^-)}\right]\right\} \qquad (6)$$

Adding *5* and *6* and inverting we get

$$I_0/I = \frac{1 + c_1((\mathrm{OH}^-) + c_3(\mathrm{OH}^-)^2)}{1 + c_1c_2((\mathrm{OH}^-) + c_3(\mathrm{OH}^-)^2)}$$

in which

$$c_1 = k_q + K$$
$$c_3 = k_qK/(k_q + K)$$

Summary

A study has been made of the deviations from the Stern–Volmer law in the quenching of the fluorescence of (1) acridone by iodide, (2) quinine by chloride, (3) naphthionate, α-naphthylamine and β-naphthylamine by hydroxide. The first two systems show marked positive deviations and the last three negative deviations. The case of α-naphthylamine is of particular interest since in addition to the negative deviation it shows an effect explainable in the same way as the positive deviations for the first two systems.

The positive deviations are explained as due to the presence of a quencher molecule in the same solvent cage as the fluorescer molecule at the moment of excitation. On the basis of this model an equation is derived which takes into account the fact that some of the activated fluorescer–quencher pairs may fluoresce.

Negative deviations from the Stern–Volmer law are explained by the assumption that the quencher molecules react with the photoactivated fluorescer molecules to form a new activated species which emits light of a different energy distribution from that emitted by the original fluorescer molecule. The distribution of the emitted energy with respect to frequency has been determined for the fluorescence both in the absence and presence of the quencher. The results obtained support the theory.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. V. Measurement of the Dielectric Constant and Loss of Low-loss Solutions[1]

BY W. M. HESTON, JR., A. D. FRANKLIN, E. J. HENNELLY AND C. P. SMYTH

The investigations of the twenty-seven liquid organic halides reported and discussed in the first three papers[2,3,4] of this series made apparent the desirability of measuring selected molecules in dilute solution in a variety of different solvents. The present paper describes the experimental method employed in these measurements and gives examples to illustrate the data obtained.

Experimental Method

The high dielectric loss method presented in the first two papers[2,3] made use of the large variation in the reflection coefficient as the sample length was changed. The absolute magnitude of the reflection coefficient for low-loss dielectrics, however, is very close to unity since power absorption by the dielectric-filled waveguide section is relatively small. Because the variation in reflection coefficient with sample length is very small and thus difficult to measure with any degree of reliability, an alternative approach has been adopted. The voltage standing wave ratio, *SWR*, is quite sensitive to small changes in dielectric loss since for low loss dielectric the *SWR* is large. The *SWR* is represented in equation (1) as

$$\rho_n = SWR = \left|\frac{E_{\mathrm{max.}}}{E_{\mathrm{min.}}}\right|_n = \frac{1 + |G|_n}{1 - |G|_n} \qquad (1)$$

where G_n is the reflection coefficient and $E_{\mathrm{max.}}$ and $E_{\mathrm{min.}}$ are the voltages of the maximum and minimum points, respectively, at the n^{th} minimum along the line. Calculation of ρ_n for various values of G_n in the neighborhood of $G_n = 1.0$ indicates that ρ_n is very sensitive to small changes in G_n. This sensitivity of ρ_n to small changes in the reflection coefficient when near unity is used to measure the dielectric absorption of low loss systems presented in this paper. Figure 1 illustrates the variation in ρ with $|G|$.

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[1] This research was carried out with the support of the Office of Naval Research. Reproduction in whole or in part permitted for any purpose of the United States Government.

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

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

[4] Hennelly, Heston and Smyth, *ibid.*, **70**, 4102 (1948).

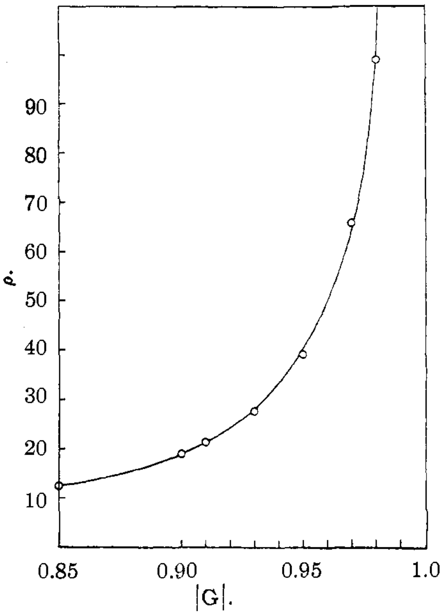

Fig. 1.—Variation in ρ with $|G|$ near unity.

The apparatus is very similar to that which is used to measure high dielectric loss materials except that the directional coupler and inductive matching diaphragm are not used, and a slotted line is employed to measure the shape of the standing wave set up in that portion of the waveguide immediately preceding the dielectric-filled cell. A diagram of the apparatus is given in Fig. 2. The 3.22 cm. and 5.59 cm. equipments have been set up in an analogous manner.

The determination of very high voltage standing wave ratios usually requires the use of calibrated attenuators because of the large variation in the signal intensity of the maximum and minimum voltage positions along the guide. Such overloading would cause non-linear response of the crystal detector and audio amplifier circuits. A second method of measuring high *SWR* is by the "width at twice minimum" method described by Surber.[5] The *SWR* may be determined by setting the detector probe at a minimum point along the guide and measuring the distances, a_1 and a_2, that the probe must be moved to double the detector output current. For a lossless line $a_1 = a_2$, and ρ will be given by

$$\rho = \left|\frac{E_{\max.}}{E_{\min.}}\right| = \frac{\lambda_g}{2\pi a_1} = \frac{\lambda_g}{\pi \Delta X} \qquad (2)$$

where λ_g is the wave length in the air-filled guide and ΔX = distance from one $\sqrt{2}\, E_{\min.}$ position to the other $\sqrt{2}\, E_{\min.}$ position. For an actual waveguide system there will be wall loss in the guide so the *SWR* will vary along the line. In the present work the wall loss has been calculated and found to be from 0.5 to 1% of the dielectric loss. If the expressions for $E_{\max.}$ and $E_{\min.}$ are evaluated and placed in the equation for ρ, the following result is obtained

$$\rho = \left|\frac{E_{\max.}}{E_{\min.}}\right| = \frac{\left[\left|\frac{E_x}{E_{\min.}}\right|^2 - \cos^2\theta\right]^{1/2}}{\sin\theta} \qquad (3)$$

where $\theta = \pi\Delta X/\lambda_g$ and E_x is $\sqrt{2}\, E_{\min.}$ If one assumes that the meter reading is proportional to E^2 and ΔX is small, then one can approximate $\cos^2\theta = 1$ and $\sin\theta = \theta$, to obtain

$$\rho = \lambda_g/\pi\Delta X \qquad (4)$$

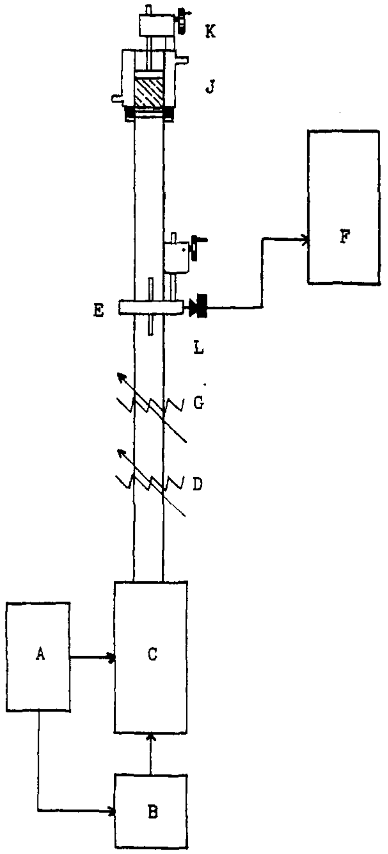

Fig. 2.—Apparatus for measurement at 1.27 cm.: (A) regulated power supply, (B) modulator, (C) 2K33 oscillator, (D) decoupling attenuator, (E) traveling detector, (F) audio amplifier, (G) power level set attenuator, (J) thermostated cell, (K) micrometer drive mechanism, (L) 1N26 crystal detector.

Equation (4) thus corresponds to equation (2) for a lossless line. The assumption that ΔX is small relative to λ_g is important and places a limit on the highest value of the dielectric loss, ϵ'', which can be measured by this method. In the present work, however, the equation for ρ was solved using the values of $\cos^2\theta$ and $\sin\theta$ for different values of ΔX and plotted on a graph of $2/\rho\pi\lambda_g$ against ΔX. At each minimum in the dielectric-filled cell the value of ΔX was recorded and from this the value of the above factor, $2/\rho\pi\lambda_g$, hereafter called "q," was obtained. A plot of q *vs.* the number of the minimum from the dielectric-mica interface will give a straight line whose slope when multiplied by λ_0^2/λ_d gives the value of ϵ'' for the dielectric and waveguide system. Calculations indicate that the assumptions made in obtaining equation (4) are valid only for values of ΔX less than 6.5% of λ_g. Accordingly, all values of ϵ'' reported herein have been calculated by use of equation (3).

Since the values of ϵ'' measured in the solution work are small, the real part of the dielectric constant, ϵ', may be obtained by measurement of the difference between successive minima in the dielectric-filled cell using the micrometer drive to vary the plunger depth and thus the sample length. The expression for ϵ' is, therefore

$$\epsilon' = (\lambda_0/\lambda_d)^2 + (\lambda_0/\lambda_c)^2 \qquad (5)$$

where λ_0 is the free space wave length, λ_d is the wave length in the dielectric-filled guide of the cell, and λ_c is the cut-off wave length in the air-filled guide. The validity of this

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(5) Surber, Technical Report No. 1, ONR Contract N 6 ori-105, Task Order IV, p. 26; Montgomery, "Technique of Microwave Measurements," McGraw-Hill Book Co., Inc., New York, N. Y., 1947, Chap. 10.

assumption that ϵ' is unaffected appreciably by ϵ'' can be demonstrated. The dissipation factor, D, is represented by equation (6)

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

Representative values of ϵ'' and ϵ' for the solution work are 0.030 and 2.10, respectively, and $(\lambda_0/\lambda_c)^2 = 0.36$. With these values $D = 0.017$. The value of ϵ' is changed by an amount which is much less than the experimental error as shown by the rigorous expression for ϵ'

$$\epsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \frac{2}{(1 + (1 + D^2)^{1/2})} \qquad (7)$$

For values of $D < 0.1$, equation (5) correctly represents the value of ϵ' and indicates that ϵ' and ϵ'' may be measured independently. The value of the factor q was obtained from the following considerations: For open circuit termination of dielectric lengths for which $n = 1, 2, 3, \ldots$

$$1/\rho_n = 1/Z_d \tanh (n\alpha\lambda_d/2) + 1/R_{oc} \qquad (8)$$

where $Z_d = \lambda_d/\lambda_g$, α = total attenuation = $(\alpha_g + \alpha_d)$, and R_{oc} = experimentally measured values of the open circuit plunger resistance.

The total attenuation, α, is made up of two parts, the attenuation due to wall loss, α_g, which is calculated from the geometry of the cell and the known conductivity of the cell walls,[5] and the attenuation due to dielectric loss, α_d. In the above equation for $1/\rho_n$, tanh $(n\alpha\lambda_d/2)$ can be approximated by tanh $(n\alpha\lambda_d/2) = n\alpha\lambda_d/2$ since α is very small and thus tanh $(n\alpha\lambda_d/2)$ is small. Therefore, equation (8) can be justifiably simplified to

$$1\rho_n/ = (1/Z_d)(n\alpha\lambda_d/2) + \text{constant} \qquad (9)$$

Rearrangement for evaluation of α results in

$$\alpha = \frac{2Z_d}{\lambda_d} \frac{\delta(1/\rho_n)}{\delta_n} \qquad (10)$$

The constant term in equation (9) includes the effect of system losses and is eliminated by plotting several values of $(1/\rho_n)$ *vs.* n as shown in Fig. 3. ϵ'' can be determined if α_d, λ_0 and λ_d are known. Thus

$$\epsilon'' = (1/\pi)(\lambda_0^2/\lambda_d)\alpha_d \qquad (11)$$

Equation (10) is substituted in equation (11) and ϵ'' is given in terms of ρ_n, λ_d, λ_0, and λ_g, since $Z_d = \lambda_d/\lambda_g$.

$$\epsilon'' = (1/\pi)(\lambda_0^2/\lambda_d)(2Z_d/\lambda_d)\ [\delta(1/\rho_n)/\delta_n] \qquad (12)$$

Finally

$$\epsilon'' = (2/\pi)(\lambda_0^2/\lambda_d\lambda_g)[\delta\ (1/\rho_n)/\delta_n] \qquad (13)$$

Therefore, the slope of $(1/\rho_n)$ *vs.* n, when multiplied by $(1/\pi)(\lambda_0^2/\lambda_d)(Z_d)$ will yield ϵ'', since the slope is $\alpha\lambda_d/2Z_d$. For convenience in the calculations, $(2/\rho_n\pi\lambda_g)$ has been plotted *vs.* ΔX since π and λ_g are constants. The slope of $q(q_n = 2/\rho_n\pi\lambda_g)$ *vs.* n multiplied by (λ_0^2/λ_d) gives the total loss ϵ'' due to dielectric absorption and wall loss. The method of plotting takes into account all system loss up to the dielectric cell, but wall loss within the cell must be considered. Equation (11) is usually written as

$$\epsilon'' = \frac{1\lambda_0^2}{\pi\lambda_d}[\alpha - \alpha_g] \qquad (14)$$

since $\alpha = (\alpha_g + \alpha_d)$. Equation (14) then takes the form

$$\epsilon'' = \frac{\lambda_0^2}{\pi\lambda_d}\left[\frac{2}{\lambda_g}\frac{\delta(1/\rho_n)}{\delta n} - \alpha_g\right] \qquad (15)$$

or

$$\epsilon'' = (\lambda_0^2/\lambda_d)(\delta q/\delta n) - d_g/\pi) \qquad (16)$$

To illustrate the complete method of calculation the results of the 30° determination of 0.0256 mole fraction t-butyl chloride in cyclohexane are presented in Table I.

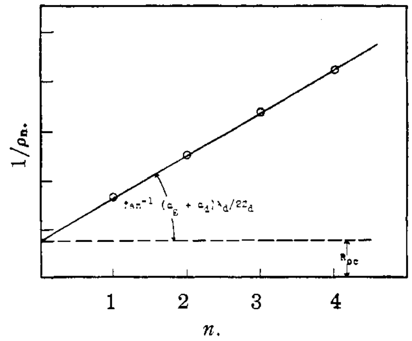

Fig. 3.—Variation of total loss with length of sample.

TABLE I

t-C_4H_9Cl IN C_6H_{12} AT 30°

$dq/dn = 0.0162$; $\lambda_0 = 1.279$ cm.; $\lambda_d = 0.9665$ cm.; $\lambda_c = 2.123$.

n	ΔX	q	Plunger	$\lambda_d/2$
1	0.0153	0.0300	10.8930	....
2	.0231	.0455	10.4095	0.4835
3	.0310	.0615	9.9262	.4833
4	.0400	.0790	9.4432	.4830
5	.0485	.0945	8.9600	.4832

From equation (5)

$$\epsilon' = (1.279/0.9665)^2 + 0.362 = 2.109$$

From equation (16)

$$\epsilon'' = \frac{(0.0162)(1.634)}{0.9665} - \frac{(0.000415)(1.634)}{\pi(0.9665)}$$

or

$$\epsilon'' = 0.0274 - 0.00022 = 0.0272$$

Therefore, tan $\delta = \epsilon''/\epsilon' = 0.0272/2.109 = 0.0129$.

Some measurements have also been completed with the 10-cm. coaxial short-circuited line method employed by Mr. F. H. Branin.[6] The same general approach to the problem of measurement of low-loss dielectrics as was utilized in the waveguide methods is used here. The only differences are: (1) the equations for coaxial transmission lines must be substituted, and, (2) a calibrated attenuator is used to measure the width of the minimum at the two points corresponding to double the minimum power. The width of each minimum expressed in fractional wave lengths is plotted as a function of the ordinal number of each minimum. The slope of this line is approximately $^1/_2$ tan δ, but must be corrected for the inner conductor losses. A complete description of the apparatus and experimental method employed at 10 cm. will be published in the near future.

Experimental Results

The method just described has been used to measure the dielectric constants, ϵ', and losses, ϵ'', of a large number of dilute solutions at different temperatures and wave lengths. The static dielectric constants, ϵ_0, have been measured with a heterodyne beat apparatus[7] at a wave length of 577 meters for use in the interpretation of the microwave frequency data. The results are illustrated by the data in Table II for solutions of ethyl bromide in n-hexadecane, the mole fraction, c_2, of the polar solute being given in the

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[6] Branin, Ph.D. dissertation, Princeton University, 1950.

[7] Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

TABLE II

DIELECTRIC CONSTANTS AND LOSSES AT 3.22 CM. OF SOLUTIONS OF ETHYL BROMIDE IN *n*-HEXADECANE

c_2	t, °C.	ϵ'	ϵ''
0.0000	20	2.051	0.0000
	30	2.039	.0000
	40	2.026	.0000
.0198	20	2.077	.0060
	30	2.065	.0050
	40	2.052	.0040
.0450	20	2.111	.0125
	30	2.095	.0104
	40	2.080	.0082
.0600	20	2.132	.0166
	30	2.116	.0144
	40	2.101	.0122
.0816	20	2.163	.0226
	30	2.146	.0197
	40	2.128	.0168

first column. The data are plotted against concentration in Figs. 4 and 5.

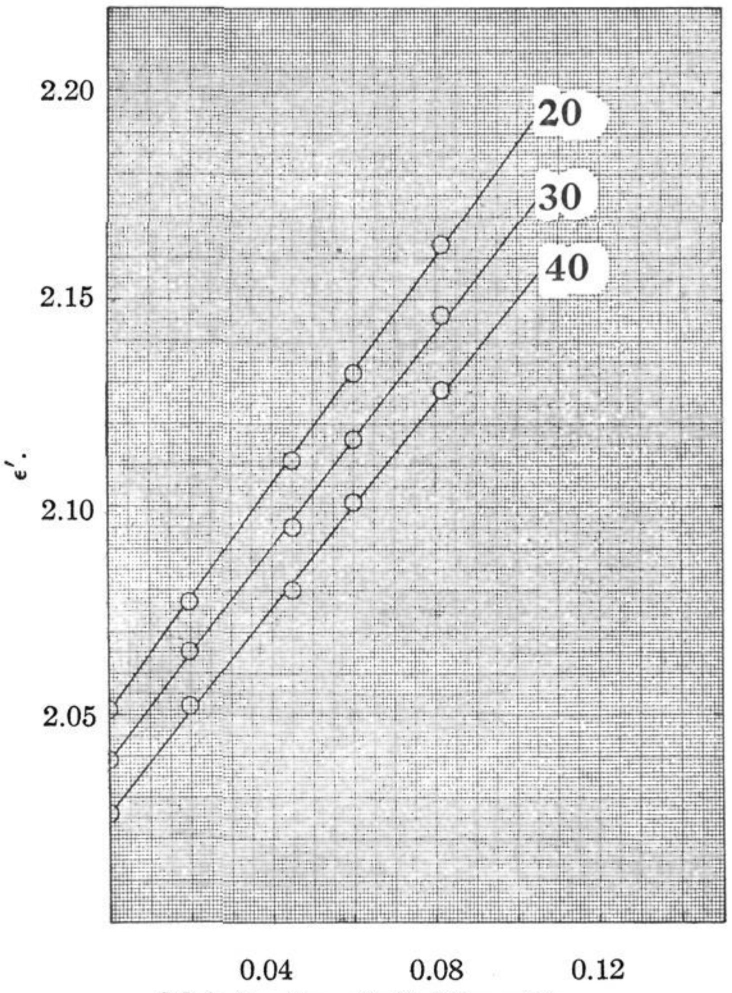

Fig. 4.—Dependence upon concentration of the dielectric constants of solutions of ethyl bromide in *n*-hexadecane at 3.22 cm.

Discussion of Results

None of the several series of dilute solutions which have been measured in the present work show any measurable departure of either the static dielectric constant, the real part of the high-frequency dielectric constant, or the loss from linear dependence upon mole fraction. This is consistent with the great body of data in the literature for static dielectric constant[8,9] and with recent measurements of the loss factors, ϵ''/ϵ', of solutions.[10,11,12] Any loss associated with the pure non-polar solvent is so small as to be negligible in comparison with the losses of the solutions. It is evident that the dielectric constants and losses of the solutions may be represented by the empirical equations

$$\epsilon_0 = \epsilon_1 + a_0 c_2$$
$$\epsilon' = \epsilon_1' + a' c_2$$
$$\epsilon'' = a'' c_2$$

in which subscript 1 refers to the pure solvent and a is the slope of the straight line.

The results of a large number of measurements upon dilute solutions carried out by this method at wave lengths of 1.277, 3.22, 5.59 and 10.00 cm. will be presented and discussed in the sixth paper of this series.

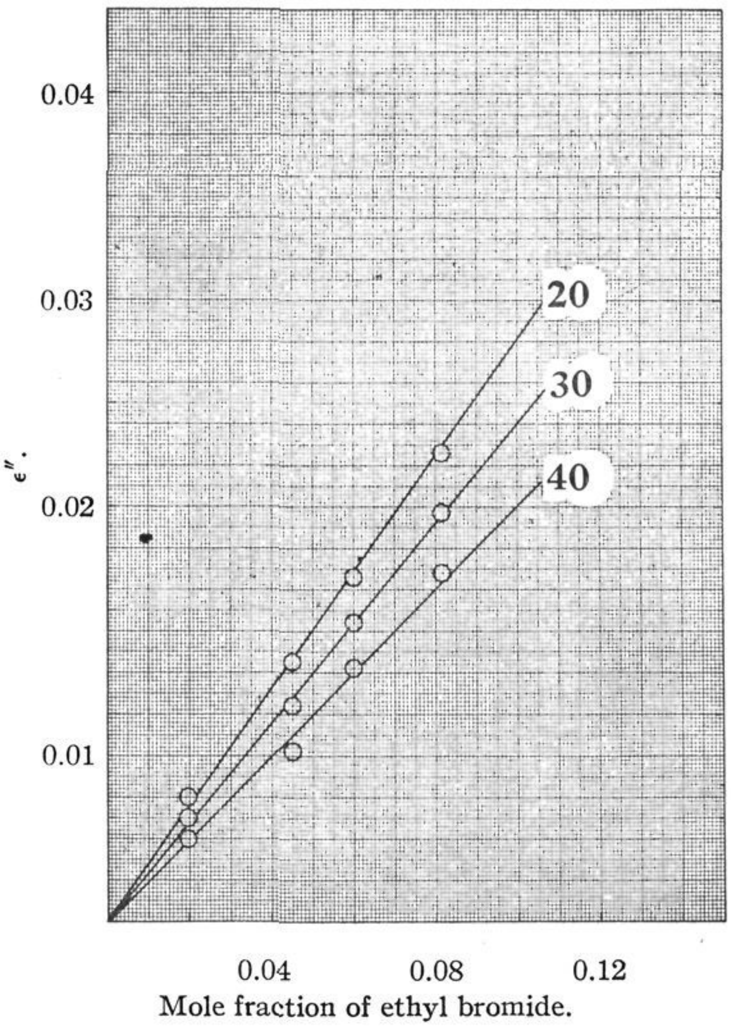

Fig. 5.—Dependence upon concentration of the dielectric losses of solutions of ethyl bromide in *n*-hexadecane at 3.22 cm.

Summary

A "width at twice minimum" standing wave ratio method is described for the measurement of the dielectric constants and losses of low-loss

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[8] Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

[9] Halverstadt and Kumler, THIS JOURNAL, **64**, 2988 (1942).

[10] Jackson and Powles, *Trans. Faraday Soc.*, **42A**, 101 (1946).

[11] Whiffen and Thompson, *ibid.*, **42A**, 114 (1946).

[12] Whiffen, THIS JOURNAL, **70**, 2455 (1948).

liquids at microwave frequencies. Measurements made at wave lengths of 1.277, 3.22, 5.59 and 10.00 cm. and 577 m. show that, for dilute solutions containing less than 0.1 mole fraction of polar organic solute in non-polar solvent, both the real part and the imaginary part of the complex dielectric constant, as well as the static dielectric constant, are linear functions of the solute concentration.

PRINCETON, NEW JERSEY RECEIVED NOVEMBER 16, 1949

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. VI. Dielectric Relaxation of Four Organic Halides and Camphor in Different Solvents[1]

BY A. D. FRANKLIN, W. M. HESTON, JR., E. J. HENNELLY AND C. P. SMYTH

The third paper[2] of this series showed that the dielectric behavior of twenty-seven liquid organic halides was represented fairly satisfactorily by the Cole and Cole empirical modification[3] of the Debye equations. For those molecules which were approximately spherical in shape, the unmodified Debye equations accurately represented the behavior of the liquids. A close parallelism was observed between the processes of dielectric relaxation and viscous flow in the liquids. Since dielectric relaxation time depends upon the viscosity of the medium as well as upon molecular size and viscosity depends upon molecular size, the effects upon dielectric behavior of molecular size and shape on the one hand and of viscosity on the other could not be adequately distinguished from one another. For this reason, it seemed desirable to measure a few polar molecules of different sizes and shapes in solution in non-polar solvents of different viscosities and different molecular sizes and shapes. The fifth paper[4] of this series described the measurement of the dielectric constants and losses of these solutions and showed for typical cases that, in accordance with general experience, these quantities were linear functions of the concentration in dilute solution. The present paper summarizes the results of a large number of measurements and attempts to draw conclusions from them.

Experimental Results

The purification of the non-polar solvents employed has, except for hexadecane, been described in the fourth paper[5] of this series, while that of the polar solutes, except camphor, is described in another paper.[6] Hexadecane from the Paragon Testing Laboratories, after a mere vacuum distillation, was found to have a considerable dielectric loss at 3.22 cm. It was, therefore, subjected to a vacuum of 1–5 mm. for an hour, and, after the addition of sodium wire, was subjected to the vacuum again for twenty-four hours. After prolonged refluxing over the sodium wire, it was distilled at a pressure lower than 1 mm. The resulting product showed no loss, but the refractive index, $n^{20}\text{D}$ 1.4366, was considerably higher than the value, 1.4344, given in the literature.[7] It was, however, satisfactory for use as a solvent. *d*-Camphor from the General Chemical Company was purified by slow sublimation.

Since it has been shown,[4] that, for the dilute solutions under discussion, the static dielectric constant, ϵ_0, the real part, ϵ', of the complex dielectric constant, and the imaginary part or dielectric loss, ϵ'', are linear functions of the concentration, the large body of experimental data on these solutions may be represented in terms of the constants in the equations

$$\epsilon_0 = \epsilon_1 + a_0c_2 \quad (1)$$

$$\epsilon' = \epsilon_1' + a'c_2 \quad (2)$$

$$\epsilon'' = a''c_2 \quad (3)$$

in which subscript 1 refers to the pure solvent, c_2 is the mole fraction of polar solute, a is the slope of the straight line for the dependence of the dielectric quantity upon the concentration. Because of the absence of appreciable loss in the non-polar solvents, $\epsilon_1' = \epsilon_1$.

The average deviation in measurement of the ϵ_0 and ϵ' values was about ±0.2% and that of the ϵ'' about 3%. However, because of the smallness of the differences, $\epsilon_0 - \epsilon_1$ and $\epsilon' - \epsilon_1'$, the average deviations of the slopes a_0 and a' are magnified to about ±5%. The average deviations in the values of a'' were also observed to be about ±5%. These average deviations, da, in the slopes were calculated from the data with the equation

$$da = \sum_{n} \Delta\epsilon_n / \sum_{n} c_n$$

in which c_n = solute mole fraction of the n^{th} sample, and $\Delta\epsilon_n = \epsilon_n - (\epsilon_1 + ac_n)$, with $\epsilon_1'' = 0$.

Table I lists the slopes a_0, a' and a'', of the linear concentration curves of the dielectric constants and loss, ϵ_0, measured at a wave length of 577 m.,

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[1] This research supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] Hennelly, Heston and Smyth, THIS JOURNAL, **70**, 4102 (1948).

[3] Cole and Cole, *J. Chem. Phys.*, **9**, 341 (1941).

[4] Heston, Franklin, Hennelly and Smyth, THIS JOURNAL, **72**, 3443 (1950).

[5] Heston and Smyth, *ibid.*, **72**, 99 (1950).

[6] Heston, Hennelly and Smyth, *ibid.*, **72**, 2071 (1950).

[7] Doss, "Physical Constants of the Principal Hydrocarbons," The Texas Company, 1942.