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, $n^{20}\mathrm{D}$ 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

$$\epsilon_0 = \epsilon_1 + a_0c_2 \tag{1}$$

$$\epsilon' = \epsilon_1' + a'c_2 \tag{2}$$

$$\epsilon'' = a''c_2 \tag{3}$$

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.,

---

[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.

TABLE I

SLOPES FOR DEPENDENCE OF DIELECTRIC CONSTANTS AND LOSS UPON CONCENTRATION

t, °C.	a_∞	a_0	λ_0	a'	a''
0	$C_2H_5Br-C_6H_6$		1	3.35	1.75
	−0.06	5.40	3	4.98	1.46
20	− .06	5.20	1	3.40	1.54
			3	4.68	1.06
40	− .07	5.00	1	3.35	1.31
			3	4.26	0.78
0	$C_2H_5Br-C_7H_{16}$		1	3.10	.78
	.15	3.10	3	3.08	.48
20	.14	3.00	1	2.80	.66
			3	2.76	.36
40	.13	(2.90)	1	2.40	.56
			3	2.49	.27
0	$C_2H_5Br-C_6H_{12}$		1	2.85	1.10
	.14	4.50	3	4.05	0.80
20	.13	4.30	1	2.85	.95
			3	3.73	.60
40	.12	4.10	1	2.80	.81
			3	3.39	.45
20	$C_2H_5Br-C_{16}H_{34}$		1	1.20	.33
	.04	1.45	3	1.37	.28
30	.04	1.40	1	1.08	.29
			3	1.29	.24
40	.04	1.37	1	0.95	.25
			3	1.24	.20
0	$C_8H_{17}Br-C_7H_{16}$		1	1.00	.70
	.34	3.44[8]	3	1.97	1.04
			5	2.80	0.80
			10	2.80	.78
20	.33	3.14[8]	1	1.20	.73
			3	1.96	.92
			5	2.68	.72
			10	2.80	.63
40	.32	2.89[8]	1	1.40	.76
			3	1.99	.81
			5	2.54	.62
			10	2.70	.50
60	.30	2.66[8]	1	1.60	.73
			3	1.96	.72
			5	2.44	.53
			10	2.65	.38
0	$C_8H_{17}Br-C_6H_{12}$		3	1.82	1.29
	.33		5	3.54	1.19
20	.30	4.20	1	1.40	1.02
			3	2.04	1.21
			5	3.14	1.10
40	.30	3.90	1	1.60	1.06
			3	2.23	1.10
			5	2.76	1.01
60		3.60	1	1.80	1.10
20	$C_8H_{17}Br-C_{16}H_{34}$		1	0.35	0.27
	.10	1.50	3	.73	.40
			5	1.04	.41
40	.10	1.40	1	0.40	.33
			3	.78	.37
			5	1.00	.36
60	.10	1.30	1	0.44	.36
			3	.79	.35
			5	.96	.32
0	$t-C_4H_9Cl-C_7H_{16}$		1	3.45	.93
	.22	4.00[9]	3	3.74	.56
			5	3.70	.34
20	.20	3.56[9]	1	2.90	.78
			3	3.50	.45
			5	3.50	.26
40	.19	3.26[9]	1	2.45	.64
			3	3.10	.34
			5	3.28	.19
20	$t-C_4H_9Cl-C_6H_{12}$		1	3.90	1.26
	.16	5.00	3	4.78	0.74
			5	4.82	.42
30	.16	4.80	1	3.90	1.12
			3	4.48	0.66
			5	4.54	.37
40	.16	4.65	1	3.85	.97
			3	4.08	.57
			5	4.26	.31
20	$t-C_4H_9Cl-C_{16}H_{34}$		1	1.70	.50
	.06	1.85	3	1.64	.27
30	.06	1.80	1	1.60	.43
			3	1.54	.24
40	.05	1.70	1	1.55	.36
			3	1.46	.22
20	$\alpha-C_{10}H_7Br-C_7H_{16}$		1	0.90	.59
	.69	2.35	3	1.78	.85
			10	2.20	.36
21	$C_{10}H_{16}O-C_6H_{12}$		1	4.03	3.53
	.21	(9.70)[10]	3	7.70	3.29
			5	8.66	1.88

and ϵ' and ϵ'', measured at 1.277, 3.22, 5.59 and 10.00 cm. as indicated in the fourth column. It also lists the values of the slope, a_∞, of the linear curve for the dependence upon concentration of ϵ_∞, the optical dielectric constant. These values are calculated from molar refraction as a linear function of concentration. They are so small that any errors in them are negligible in comparison with those in the values of the other slopes. The values of a_0 for *n*-octyl bromide in heptane are estimated from data in the literature for solutions in hexane and those for *t*-butyl chloride in heptane are calculated from previously published measurements made in this Laboratory. Table II gives the values of the static dielectric constants, ϵ_1, of the solvents, their densities d_1, and the slopes, b, of the linear curves, $d = d_1 + bc_2$, for the dependence of the density, d, upon the mole fraction, c_2. The solutes are given under b with the corresponding solvents at the left. The densities were measured in connection with viscosity measurements, which were ultimately abandoned when it became apparent that the viscosity changes in the dilute solutions were too small to have a measurable effect upon the dielectric behavior.

---

(8) Henrion, *Bull. Soc. Roy. Sci. Liège*, **8**, 37 (1939).

(9) Smyth and Dornte, THIS JOURNAL, **53**, 545 (1931).

(10) Calculated with the dilute solution approximation to Debye's equation and a value, 3.00 × 10^{-18}, for the dipole moment of the camphor molecule.

TABLE II

STATIC DIELECTRIC CONSTANTS AND DENSITIES OF SOLVENTS, AND SLOPES FOR DEPENDENCE OF SOLUTION DENSITIES UPON CONCENTRATION

t, °C.	Solvent	ϵ_1	d_1	Solution slopes, b C_2H_5-Br	C_8H_{17}-Br	α-$C_{10}H_7Br$
0	C_6H_6	(2.336)	(0.9001)	0.50		
20		2.285	.8785	.48		
40		2.245	.8573	.46		
60		2.205				
0	n-C_7H_{16}	1.951	.7012	.38	0.50	
20		1.923	.6838	.37	.51	0.80
40		1.895	.6665	.37	.50	
60		1.866	.6490		.50	
0	C_6H_{12}	(2.060)	.7985	.48	.48	$C_{10}H_{16}O$
20		2.026	.7795	.46	.50	0.26
40		1.992	.7604	.45	.50	
20	n-$C_{16}H_{34}$	2.049	.7740	.17	.19	
40		2.027	.7597	.17	.19	
60		2.004	.7454		.19	

Discussion of Results

Such microwave measurements as have been made previously upon solutions of polar organic molecules in non-polar solvents have consisted, for the most part, of loss tangent measurements, without any separation of the real and imaginary parts of the complex dielectric constant. In order to make possible a comparison of our loss measurements with those in the literature, the slopes of the loss tangent, $\tan \delta = \epsilon''/\epsilon'$, reported by Whiffen and Thompson[11,12] for α-bromonaphthalene in n-heptane and for d-camphor in cyclohexane, have been plotted against the logarithm of the wave length, the curve for α-bromonaphthalene in n-heptane being given in Fig. 1. The curves are calculated by means of the Debye equation,[13] in which the values of the relaxation time and dipole moment obtained by Whiffen and Thompson are used. Their experimental points and those obtained in the present work are plotted for comparison, their weight concentrations having been converted to mole fractions. In Fig. 1 the experimental points of both investigations lie well on the curve except at the 1.27 cm. wave length, where our point is appreciably below the curve. The agreement is equally good for the camphor curve except again at 1.27 cm., where Whiffen's point is somewhat below the curve and ours is considerably below. From these curves alone, one might draw the conclusion that our measurements are in excellent agreement with those of the other investigators except for those made with the 1.27 cm. apparatus, which might be suspected of giving too low loss values. However, the many other data reported in Table I show no such consistent discrepancy among themselves when examined by the arc plot method. Change of the values of the constants used in the curve calculations makes it possible to curve-fit either set of data equally well within the experimental error, so that it is impossible to choose one or the other as the better.

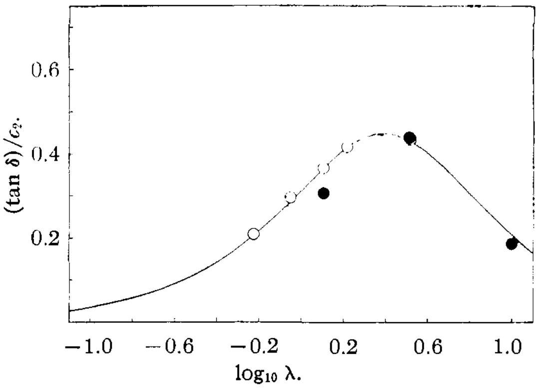

Fig. 1.—Dependence of $(\tan \delta/c_2)$ upon the logarithm of the wave length for solutions of α-bromonaphthalene in n-heptane at 20°. Hollow circles represent measurements of Whiffen and Thompson, filled circles those of the present work.

If the Cole and Cole equation,[3] represented by the arc plot, is applicable to the solutions, the values of the dielectric constant and loss for any particular solution should fit into it. Since it has been shown that each value is given by a linear equation, such as equations (1), (2), and (3), ϵ_0, ϵ', ϵ'', and ϵ_∞ in the Cole and Cole equation can be replaced by $\epsilon_1 + a_0c_2$, $\epsilon_1' + a'c_2$, etc. When this is done, c_2 and ϵ_1, ϵ_1', etc., cancel out, leaving a_0, a', a'' and a_∞, the slopes, in place of ϵ_0, ϵ', ϵ'', and ϵ_∞. In other words, each individually measured quantity in the Cole and Cole equation can be replaced by slopes, each of which is the result of measurements on several solutions at a given temperature and wave length.

When these substitutions are made, the combination of the Debye equations written in the form of an equation for a circle in the third paper[2] of this series becomes

$$\left[a' - \frac{(a_0 + a_\infty)}{2}\right]^2 + a''^2 = \left[\frac{a_0 - a_\infty}{2}\right]^2 \quad (4)$$

When the values of a'' are plotted as ordinates against those of a' as abscissas, a semicircle results according to this equation. The points of intersection of the semicircle with the abscissa axis are given by $a'' = 0$, $a' = a_\infty$ and $a'' = 0$, $a' = a_0$. The plot may differ from the usual plot in which ϵ is used instead of a by occasionally having a small negative value of a_∞, but the form of the curve is the same. The semicircular plot is well illustrated by the curve in Fig. 2 for the solutions of α-bromonaphthalene in n-heptane at 20°. The points are well represented by the semicircle corresponding to equation (4), as is to be expected since the experimental data are

---

[11] Whiffen and Thompson, *Trans. Faraday Soc.*, **42A**, 166 (1946).

[12] Whiffen, THIS JOURNAL, **70**, 2452 (1948).

[13] Whiffen and Thompson, *Trans. Faraday Soc.*, **42A**, 114 (1946).

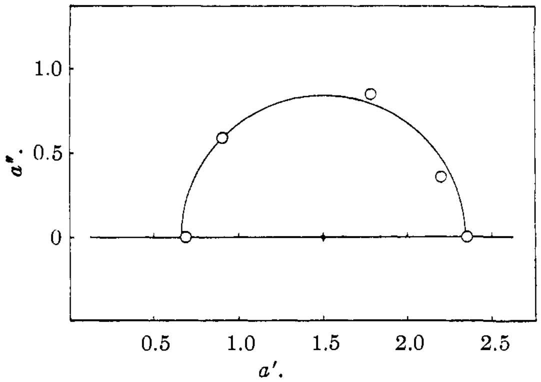

Fig. 2.—Semicircular arc plot for solutions of α-bromonaphthalene in *n*-heptane at 20°.

shown in Fig. 1 to conform well to the curve given by the Debye equation. It will be noted that, in Fig. 2, the 1.27 cm. point lies exactly on the curve in excellent agreement with the results at other wave lengths, indicating that, in spite of the apparent discrepancy of this point in Fig. 1, there is adequate agreement with our other measurements. It is evident that the Debye theory with a single relaxation time satisfactorily represents the dielectric behavior of the solutions of α-bromonaphthalene in *n*-heptane at 20°. This is in contrast to the behavior of pure α-bromonaphthalene, for which a distribution of relaxation times was observed,[2] the distribution constant α having the values 0.16 at 25° and 0.10 at 55°. The similar plot in Fig. 3 for the solutions of *n*-octyl bromide in cyclohexane at 20° shows the experimental points lying well on the arc of a semicircle but the diameter of the semicircle, represented by the straight line, is rotated through a considerable angle $\alpha\pi/2$ below the abscissa axis, α being the Cole and Cole empirical distribution constant.

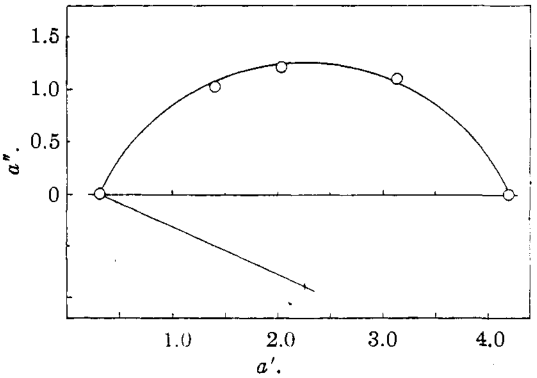

Fig. 3.—Arc plot for solutions of *n*-octyl bromide in cyclohexane at 20°.

The points for the ethyl bromide and *t*-butyl chloride solutions lie on the extreme right of the arc plots at wave lengths considerably longer than the critical wave length λ_m at which ϵ'' or a'' is a maximum. Consequently, they determine the arc and the quantities calculated from the arc with much less accuracy than that apparent in Figs. 2 and 3. Plotting of all the data shows that they fall on arc plots, but with a good deal of scatter, the divergencies being, sometimes, larger than the probable experimental errors, as is to be expected.

Cole and Cole[3] wrote the equation

$$\epsilon^* - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty)/(1 + i^{1-\alpha} f(\omega)) \qquad (5)$$

where ϵ^* is the complex dielectric constant and $f(\omega)$ is a function of the angular frequency ω. They set

$$f(\omega) = (\omega\tau_0)^{1-\alpha} \qquad (6)$$

where τ_0 is the most probable relaxation time, and showed that

$$v/u = (\omega\tau_0)^{1-\alpha} \qquad (7)$$

where v and u are the chords drawn from a point on the arc plot to the two points of intersection of the arc with the abscissa axis. It follows from simple geometrical considerations that

$$v/u = ((\epsilon_0 - \epsilon')^2 + \epsilon''^2)^{1/2}/((\epsilon' - \epsilon_\infty)^2 + \epsilon''^2)^{1/2} \qquad (8)$$

From equation (7) it follows that

$$\log (v/u) = (1 - \alpha) \log (\lambda_m/\lambda) \qquad (9)$$

or

$$\log (v/u) = -(1 - \alpha) \log \lambda + (1 - \alpha) \log \lambda_m \qquad (10)$$

since $\omega = 2\pi c/\lambda$ and $\tau_0 = \lambda_m/2\pi c$, where c is the velocity of light. It is evident that log (v/u) calculated from equation (8), when plotted against log λ, should give a straight line of slope, $-(1 - \alpha)$. Figures 4 and 5 show such plots for *n*-octyl bromide in *n*-heptane and in *n*-hexadecane, and Fig. 6 for α-bromonaphthalene in *n*-heptane at 20° and for *d*-camphor in cyclohexane at 21°. The deviations from linearity for these solutions are no greater than might be expected from the experimental errors. The negative values of the slopes, which should be equal to $(1 - \alpha)$, are given in the fourth column of Table III. The values of α obtained from the arc plots are given in the fifth column, and the values of the critical wave length, obtained graphically from these linear plots as the value of λ at which log $(v/u) = 0$, are given in the last column. The points for the ethyl bromide and *t*-butyl chloride solutions were too far from the critical wave length to warrant the linear method of plotting. For the same reason, their values of α and λ_m are approximate.

It is apparent from Table III that the slopes of the linear plots do not equal $-(1 - \alpha)$, where α is taken from the arc plots. It is possible that equation (6), which determines the slope of the linear plot but does not affect the arc plots, is not correct. The data presented here could be represented by replacing the exponent $1 - \alpha$ in equation (6) by $n(1 - \alpha)$ where n has values, for the most part, in the neighborhood of 1.3. However, it seems better, for the present, to proceed

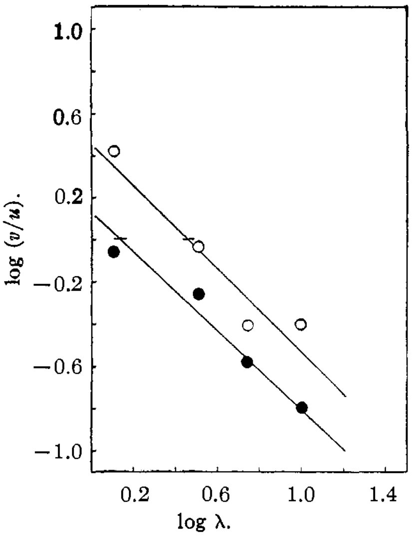

Fig. 4.—Plots of log (v/u) against log λ for solutions of *n*-octyl bromide in *n*-heptane; hollow circles, values at 0°; filled circles, values at 60°.

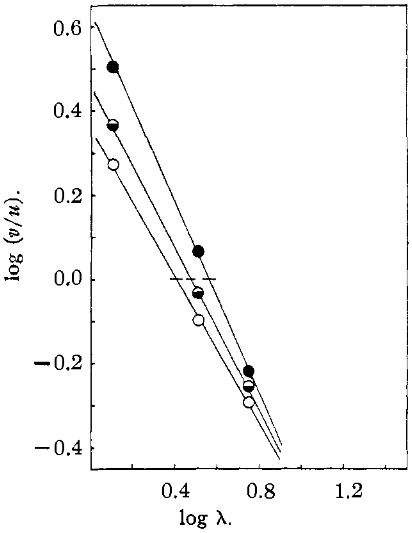

Fig. 5.—Plots of log (v/u) against log λ for solutions of *n*-octyl bromide in *n*-hexadecane; filled circles, values at 20°; half-filled circles, values at 40°; hollow circles, values at 60°.

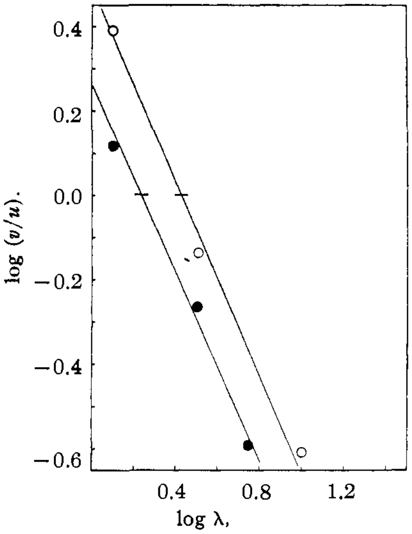

Fig. 6.—Plots of log (v/u) against log λ for solutions of α-bromonaphthalene in *n*-heptane at 20° (hollow circles) and of *d*-camphor in cyclohexane at 21° (filled circles).

on the assumption that the slopes in Table III are more in error than the values of α from the arc plots, which are based on two more points, the ϵ_∞ and ϵ_0 values, than are the linear plots.

The considerable distribution of relaxation times indicated by α for *n*-octyl bromide is in agreement with that indicated[2] for the pure liquid and is consistent with the length of the molecule, its possible existence in a variety of different shapes, and the probability of the occurrence of, at least, part of its dipole orientation by rotation around various carbon–carbon bonds in the molecular chain. Although α-bromonaphthalene in *n*-heptane and *d*-camphor in cyclohexane have both been shown to conform to the Debye equation, the former gives a semicircular plot with $\alpha = 0$ in Fig. 2, while the arc plot for the latter gives an appreciable value for

TABLE III

SLOPES, DISTRIBUTION CONSTANTS AND CRITICAL WAVE LENGTHS OF SOLUTIONS

Solute	Solvent	t, °C.	Slope	α(Arc)	λ_m, cm.
C_2H_5Br	C_7H_{16}	0		0.05	
		20		.1	0.3
		40		.26	
	C_6H_6	0		.2	
		20		.2	.6
		40		.2	
	C_6H_{12}	0		.2	
		20		.2	.4
		40		.2	
	$C_{16}H_{34}$	20		.2	.4
		30		.3	
		40		.3	
$C_8H_{17}Br$	C_7H_{16}	0	0.99	.26	2.88
		20	.95	.24	2.07
		40	.94	.24	1.82
		60	.95	.16	1.39
	C_6H_{12}	0		.28	
		20	.91	.29	3.14
		40	.63	.29	2.58
	$C_{16}H_{34}$	20	1.13	.30	3.64
		30	0.96	.39	3.00
		40	.87	.29	2.55
t-C_4H_9Cl	C_7H_{16}	0		.3	
		20		.2	.3
		40		.2	
	C_6H_{12}	20		.2	.3
		30		.3	
		40		.3	
α-$C_{10}H_7Br$	C_7H_{16}	20	1.16	.00	2.69
$C_{10}H_{16}O$	C_6H_{12}	21	1.12	.14	1.72

α. The conformity of both sets of data to Debye plots shows that the satisfactory representation of a set of experimental results by a Debye equation with a single relaxation time does not necessarily exclude the existence of some distribution of relaxation times. The very rough values of α given in Table III for ethyl bromide and *t*-butyl chloride in various solvents suggest a considerable distribution of relaxation times, although the symmetry of the molecules would lead to the expectation of only a small distribution for ethyl bromide, as observed for the pure liquid,[2] and a negligible one for *t*-butyl chloride, as observed for pure *t*-butyl bromide.[2] The uncertainty of these α values because of the location of the experimental points on the arc plots necessitates postponement of any conclusion as to their significance.

The values of the critical wave length show the usual decrease with increasing temperature, the four values for *n*-octyl bromide in heptane showing the required linear dependence of the logarithm upon the reciprocal of the absolute temperature.

In Table IV are assembled critical wave lengths at 20° from our work, from previous measurements[14] in this Laboratory, and calculated from the work of Whiffen and Thompson,[11] and from a manuscript which Dr. Whiffen has very kindly made available to us. The second and third columns give the viscosities and critical wave lengths of the pure solutes listed in the first column when the critical wave lengths are available. The subsequent columns give the critical wave lengths of the solutions in the solvent listed at the top of each column. The viscosity of each solvent is given below its formula. The viscosity values are interpolated to 20° from measurements made in this laboratory or taken from Lange's "Handbook of Chemistry," 7th ed., 1949.

TABLE IV

CRITICAL WAVE LENGTHS (CM.) AND VISCOSITIES (MILLIPOISES) AT 20°

Solute	Pure solute		λ_m for solutions in			
	η	λ_m	n-C_7H_{16} η = 4.16	C_6H_6 6.47	C_6H_{12} 9.7	n-$C_{16}H_{34}$ 36
Ethyl bromide	4.02	0.76[2]	0.3	0.6	0.4	0.4
n-Octyl bromide	16.5	4.6[2]	2.07		3.14	3.64
t-Butyl chloride	5.3	1.0[14]	0.3		0.3	
Chloroform	5.6	1.4[14]	0.58[11,15]	1.34[15]	0.60[15]	
Chlorobenzene	8.03	2.05[2]		1.56[15]	1.47[15]	
Bromobenzene	11.6	3.35[2]		2.00[15]	1.96[15]	
α-Bromonaphthalene	49.8	17.6[2]	2.69 2.45[11]			
d-Camphor			1.22[15]	1.79[15]	1.34[15] 1.72	

It has been shown in the third paper[2] of this series and elsewhere that the Debye equation

$$\tau = 4\pi\eta a^3/kT \qquad (11)$$

in which a is the molecular radius, k, the Boltzmann constant, and T, the absolute temperature is generally no more than a rough qualitative guide to the behavior of the relaxation time. In Table IV, the very approximate values for the critical wave lengths of ethyl bromide and *t*-butyl chloride in solution show no consistent variation from solvent to solvent, and are somewhat lower than the values for the pure polar liquids, although the viscosities of the two polar liquids are not far from that of the least viscous solvent. Indeed, throughout Table IV, the critical wave length for the pure polar liquid is higher than that for any of the solutions, although the viscosity is sometimes lower. If a solvent of viscosity much higher than that of hexadecane is used, the critical wave length becomes longer than that of the pure solute, as shown by the results of Whiffen and Thompson,[13] who find, for a dilute solution of chlorobenzene in a mixed cyclohexane–paraffin solvent of viscosity about eighty times that of cyclohexane, a critical wave length about four times that in cyclohexane and, therefore, about three times that in the pure polar liquid. For both ethyl benzoate and chlorobenzene solutions, successive additions of the viscous paraffin to the dilute solution in cyclohexane increases the viscosity some eighty-fold while increasing the critical wave length four to seven-fold. Similarly, Jackson and Powles[16] have found a relaxation time or critical wave length for benzophenone in dilute solution in medicinal liquid paraffin 18 times that in benzene, while the viscosity of the paraffin is 298 times that of the benzene. Jackson and Powles regard this result as confirming the well-recognized inadequacy of the Debye relation connecting the relaxation time of dipole orientation and the macroscopic viscosity, and Whiffen and Thompson conclude that the relaxation time is far from being proportional to the macroscopic viscosity as required by equation (11) and that η should be regarded as an internal viscosity coefficient. It was as an internal viscosity coefficient that Debye used η in deriving equation (11), but our ignorance of the internal friction or viscosity coefficient has necessitated the use of the measured viscosity as an inferior substitute.

Dr. H. L. Laquer in this Laboratory advanced reasons for the use of $\sqrt{\eta}$ instead of the first power in equation (11). The square root relationship gives a better approximation to the observed behavior than the first power, but still fails to account for some of the trends in Table IV. The decrease in critical wave length from benzene to cyclohexane solutions in Table IV, in spite of a 50% increase in viscosity, suggests a specificity in the behavior with molecular sizes and shapes playing an important part.

It has been pointed out[17] that dipole orientation, which takes place by molecular rotation, is facilitated by approach of the molecule toward

---

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

[15] Whiffen, *Trans. Faraday Soc.*, **46**, 130 (1950).

[16] Jackson and Powles, *ibid.*, **42A**, 101 (1946).

[17] Smyth, *Record of Chemical Progress*, **11**, 1 (1950).

spherical form. If the shape of the orienting molecule is close to that of a sphere, rotation can occur without any considerable displacement of the neighboring molecules, so that the critical wave length should be relatively insensitive to viscosity, a property involving translation as well as rotation of molecules. If the molecule is unsymmetrical, its rotation around one or more axes should involve the translational displacement of some of its neighbors with the result that the corresponding relaxation time should be more dependent upon the viscosity of the liquid. This could account for the absence of any considerable increase in critical wave length with increase in viscosity in the solutions of the small and relatively symmetrical molecules of ethyl bromide and *t*-butyl chloride in contrast to the considerable increase for the long *n*-octyl bromide molecule. A factor lessening the dependence of critical wave length upon viscosity when long, flexible molecules are involved is the fact that the dipole orientation may involve the translational motion of only a small segment of the long molecular chain. It is possible that the apparent tendency of the critical wave length of the pure polar liquid to be longer than that of the solution of about the same viscosity may be due to hindrance of molecular rotation by dipole–dipole interaction, which is present in the pure liquid and largely absent in the dilute solution.

The regular increase of critical wave length with the increase in molecular volume resulting from increase in chain length in the pure liquid *n*-alkyl bromides has already been demonstrated,[2] but it was also found that the increase fell farther and farther behind the increase in viscosity, presumably, because of increasing internal orientation by twisting around the carbon–carbon bond. For any given solvent in Table IV, the critical wave length shows a marked upward trend with increasing size of the solute molecule. A rough over-all indication of this trend is given by Fig. 7, in which the critical wave length values for the solutions in Table IV and other values[16,18,19] for solutions are plotted against the molar volumes of the pure liquid solutes calculated from their densities. Since the often irregular effects of the solvent viscosities cause considerable differences between the values for different solutions, the points should obviously not lie on a single curve. However, a curve is drawn merely to show the general upward trend of the critical wave length with increasing molecular volume. According to equation (11), the curve should be linear, but, in view of the manner in which it is drawn, its exact shape is not significant.

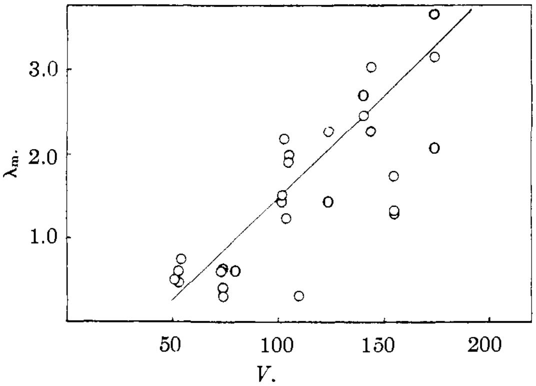

Fig. 7.—Dependence of critical wave length upon molar volume of solute.

The linear dependence of the logarithm of the critical wave length or relaxation time of *n*-octyl bromide upon the reciprocal of the absolute temperature has been used to calculate the energy of activation $E_\epsilon^\ddagger$, for the process of dipole relaxation according to the absolute rate theory.[20] The values thus obtained, together with similar quantities for the process of viscous flow of the solvents are given in Table V.

TABLE V

ACTIVATION ENERGIES (KCAL./MOLE) FOR DIELECTRIC RELAXATION AND VISCOUS FLOW OF *n*-OCTYL BROMIDE SOLUTIONS

Solvent	$E_\epsilon^\ddagger$	$E_v^\ddagger$
n-Heptane	1.8	1.9
Cyclohexane	1.9	2.8
n-Hexadecane	2.0	4.0

As usually observed, the magnitudes of the activation energies for dielectric relaxation are similar to those for viscous flow. However, the energy of activation for the dielectric relaxation of the polar solute molecule does not increase much with increase in the viscosity of the solvent in contrast to the marked increase in the energy required for the viscous flow process.

Summary

The dielectric constants and losses of solutions of polar organic molecules in non-polar solvents have been measured at temperatures between 0 and 60°, at wave lengths of 1.277, 3.22, 5.59 and 10.00 cm. and 577 m. The values of the slopes of the plots against concentration between mole fraction 0.00 and 0.07 of polar solute, are given for solutions of ethyl bromide in benzene, heptane, cyclohexane and hexadecane, of *n*-octyl bromide in heptane, cyclohexane, and hexadecane, of *t*-butyl chloride in heptane and cyclohexane, of α-bromonaphthalene in heptane, and of camphor in cyclohexane. It is shown that these empirical constants or slopes can be substituted in the Debye equations or their empirical modifications instead of single values of the dielectric constant and loss. All the results can be

---

[18] Whiffen and Thompson, *Trans. Faraday Soc.*, **42A**, 122 (1946).

[19] Cripwell and Sutherland, *ibid.*, **42A**, 149 (1946).

[20] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, Chap. IX.

adequately represented by arc plots, in which the values of the imaginary part of the dielectric constant are plotted as ordinates against those of the real part as abscissas. The critical wave lengths or relaxation times of the polar molecules tend to be longer in the pure polar liquids than in solutions of about the same viscosity and tend to increase with increasing viscosity of the solvent much less than is required by the Debye theory. They increase with molecular volume in, at least, qualitative conformity to the Debye theory.

PRINCETON, NEW JERSEY RECEIVED DECEMBER 9, 1949

[CONTRIBUTION NO. 63 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Influence of Certain Additives on the Rate of Catalytic Hydrogenation of Terpenes on Nickel

BY HILTON A. SMITH AND JOHN F. FUZEK

In a previous communication[1] it was shown that the rate of catalytic hydrogenation of some terpenes on Raney nickel catalyst was influenced by the presence of small amounts of palmitic acid. A thorough study of this phenomenon has been made, and the results are reported here.

Experimental

The terpenes were the same as those previously described.[1]

Raney nickel was prepared both by the method of Mozingo,[2] and by the method of Pavlic and Adkins[3] which is said to give a more active form.

Many of the materials tested as additives were Eastman Kodak Co. best grade chemicals, and were used without further purification. Pure **formic acid** was prepared by fractionation of 89% solution, giving the pure acid and maximum-boiling azeotrope. **Acetic, propionic, butyric and valeric acids** were purified by fractionation of reagent grade or Eastman Kodak Co. best grade acids. ***n*-Undecanoic acid** was prepared by hydrogenation of 10-undecenoic acid.[4] **Pentadecylic acid** was prepared by addition of carbon dioxide to the Grignard reagent prepared from myristyl bromide. **Nonadecylic** and **tricosanoic** acids were similarly prepared from octadecyl and *n*-docosyl bromides. **Behenic acid** was prepared by hydrogenation of Eastman erucic acid. Some of the behenic acid was converted to *n*-docosyl alcohol by reduction with hydrogen in the presence of copper chromite. This was then converted to the bromide by reaction with hydrobromic acid. **N-Tetracosanoic acid** and **arachidic acid** were prepared by a malonic ester synthesis using *n*-docosyl bromide and *n*-octadecyl bromide, respectively. **γ-Phenylbutyric acid and** ε-phenyl-*n*-**caproic acid** were prepared by carbonation of the Grignard reagents prepared from γ-phenylpropyl bromide and ε-phenylamyl bromide. **δ-Phenylvaleric acid and** ξ-phenyl**heptanoic** acid were prepared from the same bromides through malonic ester syntheses. The ε-phenylamyl bromide was prepared from γ-phenylpropyl bromide by addition of ethylene oxide to the Grignard reagent, and reaction of the resulting alcohol and anhydrous hydrogen bromide.

The **cyclohexyl-substituted acids** were all prepared by catalytic hydrogenation of the corresponding phenyl-substituted acids using Adams platinum catalyst and acetic acid as solvent.

Laurylamine and stearylamine were obtained from Armour and Co., and were fractionated prior to use. Sodium oleate was Merck U.S.P. grade chemical. **Cetyldimethylethylammonium** bromide **and** octadecyldimethyl**benzylammonium chloride** were Eastman practical grade chemicals, and were used without purification. Sodium lauryl sulfate was obtained from the Fisher Scientific Company.

The runs were carried out in a small hydrogenation bomb of the type described by Adkins.[5] The bomb had a volume of 45 ml., while the volume of the pressure gage and connections was 11 ml. The bomb was equipped with a heating jacket of conventional design, and was agitated through an angle of 30° at a rate of 42 cycles per minute. This speed has been shown to be sufficient to maintain equilibrium conditions.[1] Reactions were carried out in the manner previously described,[1] with the exception of the fact that, after the catalyst and terpene were in the bomb, a weighed amount of the additive to be tested was added before connection to the gage was made. When runs were made at elevated temperatures, the bomb was heated to the desired temperature as quickly as possible (usually not longer than fifteen minutes were required), after which shaking was commenced. In general, no reaction took place during the preliminary heating period. During an individual hydrogenation, temperatures were maintained constant to ±0.5°. After the runs were completed, the catalyst was filtered out and weighed under carbon dioxide.[1] The catalyst weights were corrected for the amount of adsorbed additive.

Experimental Calculations and Results

It has already been shown that the rates of these hydrogenations follow the equation

$$\log p^0/p = k'T/2.303V$$

where p is the pressure at any time t, p^0 is the initial pressure, V is the volume of hydrogen in the system and k' is the reaction rate constant.[1] All rate constants which are recorded here are obtained by dividing k' by the weight of catalyst used, thus referring all constants to one gram of catalyst. Table I gives a list of such constants for the hydrogenation of *d*-limonene on Standard Raney nickel catalyst in the presence of a number of additives.

Figure 1 shows the effect of varying amounts of additive on the rate constant for hydrogenation of *d*-limonene. Figure 2 shows a similar effect for varying amounts of palmitic acid on the rate constant for the hydrogenation of several terpenes. Figure 3 shows similar curves for caproic and palmitic acid using *d*-limonene and standard Raney catalyst, as well as the effect of palmitic

---

[1] Smith, Fuzek and Meriwether, THIS JOURNAL, **71**, 3765 (1949).

[2] Mozingo, *Org. Syn.*, **21**, 15 (1941).

[3] Pavlic and Adkins, THIS JOURNAL, **68**, 1471 (1946).

[4] Obtained from the Baker Castor Oil Company.

[5] Adkins, "Reactions of Hydrogen," The University of Wisconsin Press, Madison, Wisconsin, 1937, pp. 29-45.