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-chloronaphthalene, 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.

PRINCETON, NEW JERSEY RECEIVED JULY 3, 1948

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. III. Dielectric Relaxation and Structure in Organic Halides[1]

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

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 equations[4] for the dependence of dielectric constant and loss factor upon frequency are

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

and

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

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

$$x = B\omega t \qquad (3)$$

where

$$B = (\epsilon_0 + 2)/(\epsilon_\infty + 2) \qquad (4)$$

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

[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.

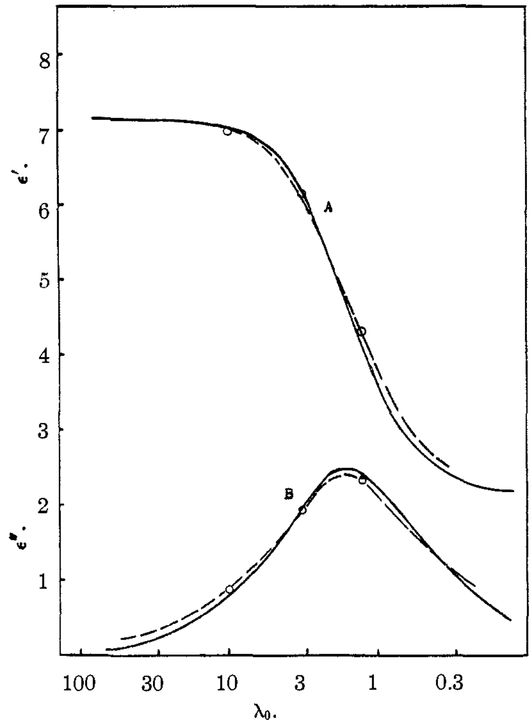

Fig. 1.—Dependence of dielectric constant (A) and loss factor (B) of *i*-butyl bromide at 25° upon the logarithm of the wave length (cm.).

through a maximum to a small value again (Fig. 1, B). Although liquids may conform to the behavior demanded by these equations, as does *i*-butyl bromide approximately in Fig. 1, the dispersion commonly occurs over a wider frequency range, with a maximum value of ϵ'' lower than that predicted by equation (2), as shown in Fig. 2. This effect has been attributed to a distribution of relaxation times. The different distribution functions for relaxation times which have been developed[5-9] have been shown[10] to give results almost indistinguishable from one another experimentally.

According to the treatment of Debye[4]

$$\tau = 4\pi\eta a^3/kT \tag{5}$$

in which the molecule is pictured as a sphere of radius, a, rotating in a medium of viscosity, η, k being the Boltzmann constant and T, the absolute temperature. This equation may be rearranged and written in the form

$$V_D = 4\pi a^3 N/3 = \tau RT/3\eta \tag{6}$$

where V_D is the hypothetical volume of the N molecules in a mole as calculated from relaxation time and viscosity measurements.

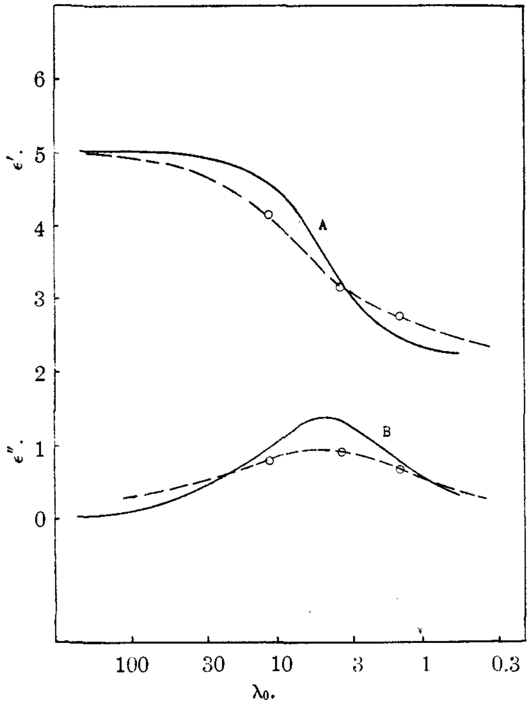

Fig. 2.—Dependence of dielectric constant (A) and loss factor (B) of *n*-octyl bromide at 25° upon the logarithm of the wave length (cm.).

For some purposes it is convenient to discuss the results in terms of the critical wave length, λ_m, the wave length corresponding to the angular frequency, ω_m, at which ϵ'' reaches its maximum value, ϵ''. Equation (2) shows that ϵ'' reaches a maximum when x equals 1, *i. e.*

$$\epsilon''_m = (\epsilon_0 - \epsilon_\infty)/2 \tag{7}$$

The corresponding value of ϵ' at the frequency ω_m for which x equals 1 is

$$\epsilon'_m = (\epsilon_0 + \epsilon_\infty)/2 \tag{8}$$

Similarly, when x equals 1

$$\omega_m = 1/B\tau \tag{9}$$

The Debye equations may be solved algebraically to give three alternative expressions for the critical wave length

$$\lambda_m = \lambda_0\left[\frac{\epsilon_0 - \epsilon'}{\epsilon' - \epsilon_\infty}\right]^{1/2} \tag{10}$$

$$\lambda_m = \frac{\lambda_0}{2}\,\frac{(\epsilon_0 - \epsilon_\infty)}{\epsilon''} \pm \frac{\lambda_0}{2}\left(\left(\frac{\epsilon_0 - \epsilon_\infty}{\epsilon''}\right)^2 - 4\right)^{1/2} \tag{11}$$

(The minus sign is used when λ_m is less than λ_0, and the plus sign when λ_m is greater than λ_0) and

$$\lambda_m = \lambda_0\,\frac{\epsilon''}{(\epsilon' - \epsilon_\infty)} \tag{12}$$

The equation for the complex dielectric constant may be written

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega B\tau} \tag{13}$$

Cole and Cole[7] have proposed an empirical relationship of the form

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(5) Wagner, *Ann. Physik*, **40**, 817 (1913); *Arch. Elektrotech.*, **3**, 83 (1914).

(6) Yager, *Physics*, **7**, 434 (1936).

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

(8) Kirkwood and Fuoss, *ibid.*, **9**, 329 (1941).

(9) Fuoss and Kirkwood, THIS JOURNAL, **63**, 385 (1941).

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

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (j\omega\tau_0)^{1-\alpha}} \qquad (14)$$

where τ_0 is the most probable relaxation time, corresponding to the frequency at which $\epsilon'' = \epsilon''_m$ and α is an empirical constant with values between 0 and 1, a measure of the distribution of the relaxation times. Equations (1) and (2) can be combined and written in the form of the equation for a circle

$$\left(\epsilon' - \frac{(\epsilon_0 + \epsilon_\infty)}{2}\right)^2 + \epsilon''^2 = \left(\frac{\epsilon_0 - \epsilon_\infty}{2}\right)^2 \qquad (15)$$

Since all values must be positive, this gives a semicircular plot of ϵ'' against ϵ', as shown in Fig. 3.

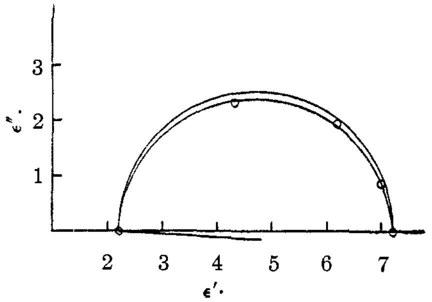

Fig. 3.—Semicircular plot of *i*-butyl bromide.

If the values of ϵ'' give a semi-circle when plotted against those of ϵ', it means that the data conform to the Debye theory. Cole and Cole[7] found that the values of ϵ'' commonly fell below the semi-circle, but could be represented by a semi-circular arc intersecting the abscissa axis at the values of ϵ_∞ and ϵ_0. The center of the circle of which this arc was a part lay below the abscissa axis and the diameter drawn through the center from the ϵ_∞ point made an angle $\alpha\pi/2$ with the abscissa axis. The arc plot is illustrated in Fig. 4 for *n*-octyl bromide.

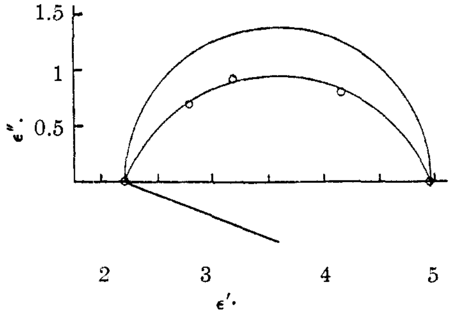

Fig. 4.—Semicircular plot of *n*-octyl bromide.

For the value of ϵ_∞ to be used in the interpretation of the dielectric constant and loss factor results, it was, at first, thought sufficient to use the square of the refractive index for the sodium D line, n^2_D. However, it soon became apparent that a consistent representation of the data could be obtained by increasing the value used for ϵ_∞ by a small amount arising from atomic polarization. The induced polarization of a substance, the sum of the atomic polarization, P_A, and the electronic polarization, P_E, is given by the expression

$$P_E + P_A = (\epsilon_\infty - 1)M/(\epsilon_\infty + 2)d \qquad (16)$$

The induced polarization is equal to the total polarization for non-polar substances, while, for polar substances, it is given by the intercept at $1/T = 0$ obtained by extrapolation of the curve for P against $1/T$ for a gas. The induced polarization found[11] for ethyl bromide, 21.50, is 2.63 higher than the value of R_D, the molar refraction for the sodium D line. The atomic polarizations found for the normal paraffins increase by about 0.07 for each added CH_2. It has, therefore, seemed a reasonable approximation to estimate $P_E + P_A$ for the alkyl bromides by adding to their molar refractions 2.63 plus 0.1 for each CH_2 added beyond ethyl bromide. The value 45.46 thus obtained for heptyl bromide is close to the 45.8 found experimentally.[12] Values for the other substances investigated were estimated by similar methods. The errors involved in the estimates are, probably, no greater than those occurring in the few available experimental data for polar substances and are not sufficient to impair the usefulness of the ϵ_∞ values calculated from them by means of equation (16). The values of ϵ_∞ and the experimentally determined refractive indices, densities and static dielectric constants, ϵ_0, will be given in another paper. These estimated values of ϵ_∞, slightly higher than n^2_D, lead to a satisfactory representation of data observed at two or three frequencies[2,3,13] with values of α from 0 to 0.3.

To determine α in the present work, it is assumed that lines drawn between adjacent plotted points are chords of a circle with its center below the real axis. The center of the circle is given by the intersection of the perpendicular bisectors of these chords and the perpendicular bisector of the abscissa axis between ϵ_∞ and ϵ_0 (Fig. 4). Tan $(\alpha\pi/2)$ is measured on the plot and α calculated from it. When values of ϵ_∞ which have been corrected for the small contribution from the atomic polarization are used, a well-described circular arc can be constructed through all the points. However, when values of n^2_D are substituted for ϵ_∞, the intersection of the three perpendicular bisectors which determine the center of the circle does not occur at a point.

The following equations were used to calculate the critical wave length and relaxation time

$$v/u = (\omega\tau_0)^{1-\alpha} \qquad (17)$$

$$\lambda_m = 2\pi c\tau_0 \qquad (18)$$

where c is the velocity of light, v the distance on the Cole and Cole plot between ϵ_0 and the 1.27 cm. point, and u the distance between the 1.27 cm. point and ϵ_∞. This shows the effect of α on τ_0. If α were zero, v/u would equal $\omega\tau_0$, which is true for the Debye equations.

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[11] Smyth and McAlpine, *J. Chem. Phys.*, **2**, 499 (1934).

[12] Smyth and McAlpine, *ibid.*, **3**, 348 (1935).

[13] Branin, unpublished measurements at 10 cm.

For convenience in discussing the dependence of ϵ' and ϵ'' upon the free space wave length, λ_0, equations (1) and (2) may be written with λ_m introduced to give

$$\epsilon' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + (\lambda_m/\lambda_0)^2) \qquad (19)$$

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)(\lambda_m/\lambda_0)/(1 + (\lambda_m/\lambda_0)^2) \qquad (20)$$

The most probable value of λ_m obtained by the method of the semi-circular plot and given in Table I can be advantageously used with the values of ϵ_0 and ϵ_∞ to calculate curves for ϵ' and ϵ'' as functions of λ_0. Isobutyl bromide has been selected for plotting in Fig. 1 since its value of α, 0.03 at 25°, is so small as to indicate virtually no distribution of relaxation times. The 25° values of ϵ' at 1.27 cm.,[2] at 3.22 cm.[3] and at 10.0 cm.,[13] as shown by the points in Fig. 1, lie on a curve which is barely distinguishable from the calculated curve. The same is true of the corresponding values for ϵ''. In other words, the dielectric behavior of isobutyl bromide is barely distinguishable, by an amount indicated quantitatively by the possession by α of a value 0.03 instead of 0, from that of a substance possessing a single relaxation time and an internal field given by the Onsager theory, which makes $B = 1$. The similar curves for *n*-octyl bromide (Fig. 2), for which α is 0.226 at 25°, show the spreading and flattening previously mentioned as characteristic of most dielectrics as the result of a distribution of relaxation times.

TABLE I

VALUES OF CRITICAL WAVE LENGTH (CM.) AND DIELECTRIC RELAXATION TIME (SEC.) OBTAINED FROM SEMICIRCULAR ARCS

Compound	1.0°C. $\tau_0 \times 10^{11}$	1.0°C. λ_m	25.0°C. $\tau_0 \times 10^{11}$	25.0°C. λ_m	55.0°C. $\tau_0 \times 10^{11}$	55.0°C. λ_m
Ethyl bromide	0.52	0.99	0.38	0.71	..	..
n-Propyl bromide	0.82	1.53	.58	1.09	0.47	0.89
i-Propyl bromide	0.67	1.26	.53	0.99	.38	0.72
n-Butyl bromide	1.12	2.11	.87	1.64	.64	1.20
i-Butyl bromide	1.04	1.96	.83	1.56	.63	1.18
s-Butyl bromide	0.91	1.72	.71	1.34	.55	1.03
t-Butyl bromide	0.82	1.55	.62	1.17	.47	0.89
n-Amyl bromide	1.77	3.33	1.21	2.28	.87	1.64
n-Hexyl bromide	2.31	4.38	1.57	2.96	1.06	2.00
n-Heptyl bromide	3.05	5.74	1.92	3.61	1.25	2.35
n-Octyl bromide	3.60	6.78	2.18	4.09	1.37	2.58
n-Nonyl bromide	4.84	9.10	2.85	5.36	1.58	2.97
n-Decyl bromide	6.92	13.10	3.37	6.32	1.91	3.60
n-Dodecyl bromide	10.20	19.20	4.89	9.20	2.44	4.59
n-Tetradecyl bromide	12.40	23.30	5.38	10.10	2.81	5.26
n-Hexadecyl bromide	...	...	6.96	13.10	3.07	5.78
n-Octyl chloride	2.72	5.12	1.71	3.22	1.03	1.94
n-Octyl iodide	6.42	12.10	3.85	7.24	2.24	4.22
n-Dodecyl chloride	6.09	11.50	3.15	5.92	1.78	3.35
Cyclohexyl bromide	3.14	5.90	1.95	3.67	1.30	2.45
Chlorobenzene	1.47	2.77	1.03	1.94	0.73	1.37
Bromobenzene	2.41	4.53	1.64	3.09	1.14	2.15
α-Chloronaphthalene	10.90	20.50	4.91	9.24	2.78	5.23
α-Bromonaphthalene	...	...	8.60	16.20	4.26	8.02
Ethylene chloride	0.97	1.83	0.70	1.31	0.45	0.85
Ethylene bromide	...	...	1.16	2.18	.76	1.43
Tetramethylene chloride	1.30	2.45	0.94	1.77	.62	1.16

Critical Wave Length

If the Debye theory fitted these liquids exactly, the three different equations (10), (11) and (12) for λ_m would, in the absence of experimental error, give identical results. Although in some cases[14] fairly good agreement may be obtained among the values obtained by the different methods of calculation, the agreement for the calculations from the data in the present paper is very unsatisfactory, except where the Cole and Cole α is very close to zero. It has seemed preferable to use equation (11) for the calculation of the values of λ_m. For measurements in the immediate vicinity of λ_m, choice as to the correct sign of the second term was made on the basis of the position of the 1.27 cm. point on the Cole and Cole arc diagram with respect to the midpoint of the line connecting ϵ_∞ and ϵ_0. If the point falls to the right of the midpoint, it indicates a value of λ_m less than λ_0; if to the left, a value of λ_m greater than λ_0. Accordingly, in the former case the minus sign is used while in the latter case the plus sign is used. A considerable error in the value for λ_m may result in this region. In Fig. 5 these values of λ_m for the straight-chain alkyl bromides calculated by means of equation (11) are plotted against the number of carbon atoms in the chain. At 1°, λ_m appears to increase linearly with the number of carbon atoms in the chain. At 25°, the rate of increase of λ_m begins to diminish appreciably for a carbon chain in the vicinity of ten atoms, while at 55° the slope begins to diminish for somewhat shorter chains.

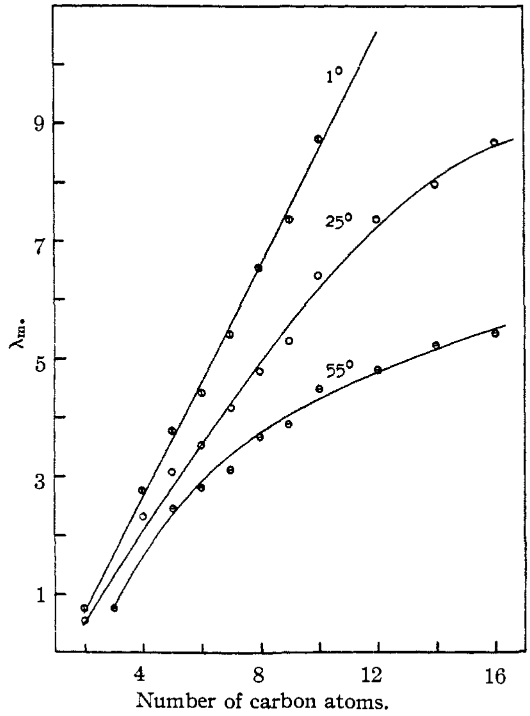

Fig. 5.—Critical wave lengths (cm.) calculated from Debye equation (11) as functions of chain length.

Since the semi-circular plots according to equation (15) showed that some correction was neces-

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

sary to take care of the existence of a distribution of relaxation times, the values of λ_m calculated by means of the Cole and Cole arcs and the use of α and equations (17) and (18) should be much more dependable than those in Fig. 5. The values of λ_m thus calculated and given in Table I along with the values of τ_0 differ appreciably from the values previously considered. The curves for λ_m against the number of carbon atoms in the molecular chain in Fig. 6 show an increasing upward slope at 1° and 25°. At 55° the curve is almost linear with a very slight decrease in slope with increasing chain length. The approximate linearity of this 55° curve is similar to that of the 1° curve for the uncorrected values in Fig. 5, but the 55° curve has a much lower slope because of the higher temperature.

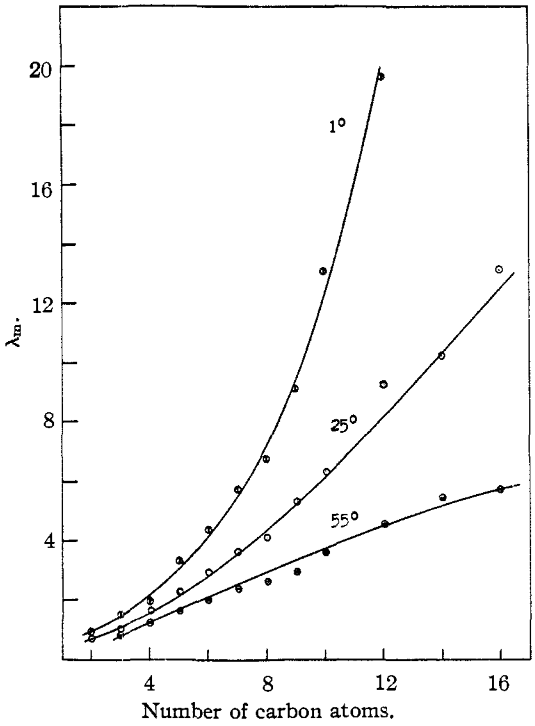

Fig. 6.—Critical wave lengths (cm.) calculated from semicircular arcs as functions of chain length.

On the basis of equation (5), τ and hence λ_m should, if the viscosity and temperature remained constant, increase linearly with a^3, which is proportional to the number of carbon atoms in the molecule. Since the viscosity, as shown by the measurements of one of the authors to be published in another paper, increases rapidly with increasing molecular size, the upward swing of the 1° and 25° curves in Fig. 6 is to be expected. The decrease in the rate of change of the slope of the the curves from positive to zero or slightly negative at 55° with increasing chain length shows that the effective a^3 is not a linear function of the number of carbon atoms. This would seem to indicate that dipole orientation may occur not only by orientation of the molecule as a whole but also by rotation around the carbon–carbon bonds of the chain. This latter type of orientation becomes increasingly possible as the number of carbon–carbon bonds increases with increasing chain length and as the temperature rises. The twisting of a portion of the molecule by rotation around a bond is hindered by neighboring molecules and may require some displacement of these molecules. Consequently, λ_m should still increase with the viscosity of the liquid even if dipole orientation were occurring wholly through internal rotation in the molecule. The close parallelism between λ_m and η is shown by the curves at 1° and 55° for the two quantities plotted against number of carbon atoms in Fig. 7 on such scales as to make the curves at each temperature as nearly coincident as possible.

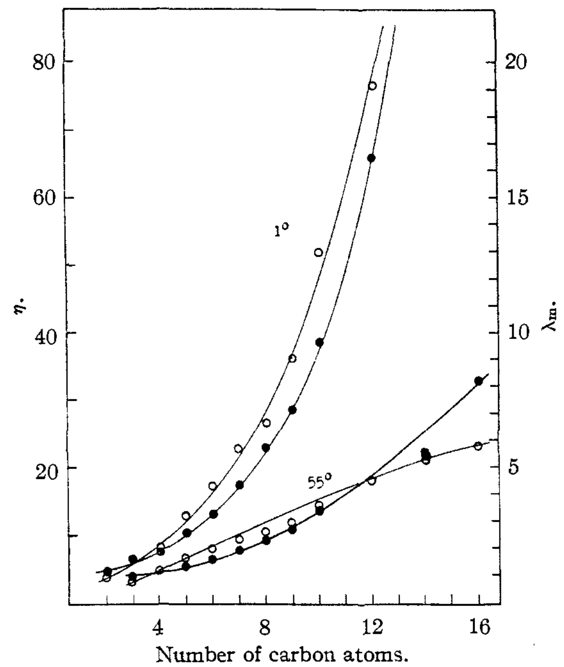

Fig. 7.—Dependence of critical wave length and viscosity upon chain length: ●, viscosity; ○, critical wave length.

The curves in Fig. 8 for the critical wave length values in Table I plotted against temperature are very similar in appearance to those in Fig. 9 representing the dependence of viscosity upon temperature, as would be expected in view of the similarity of the curves for critical wave length and viscosity plotted against number of carbon atoms.

The hypothetical molar volume, V_D, given by equation (6) may be used as a convenient function for describing the behavior of the dielectric relaxation time and the viscosity. Values previously obtained[15] for it were commonly only 10 to 20% of the directly measured molar volume, $V = M/d$, and, in some cases, even smaller. Comparison of the values of V_D in Table II calculated by means of equation (6) and plotted in Fig. 10, with the

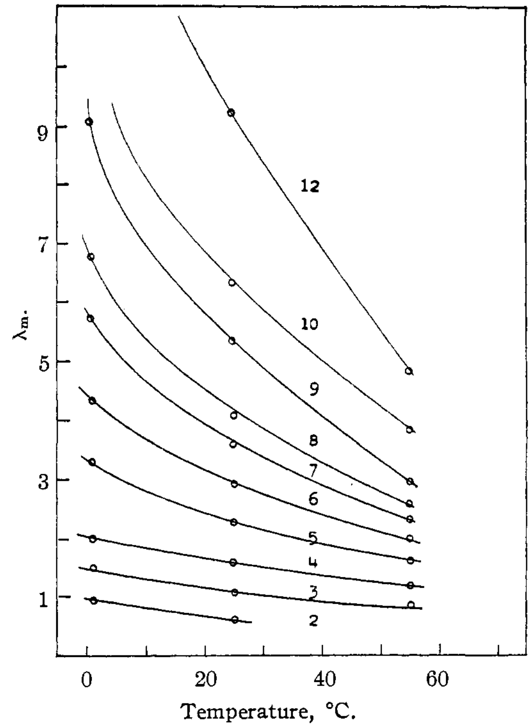

Fig. 8.—Dependence of λ_m (cm.) of the normal alkyl bromides upon temperature. The number on each curve is the number of carbon atoms in the molecule.

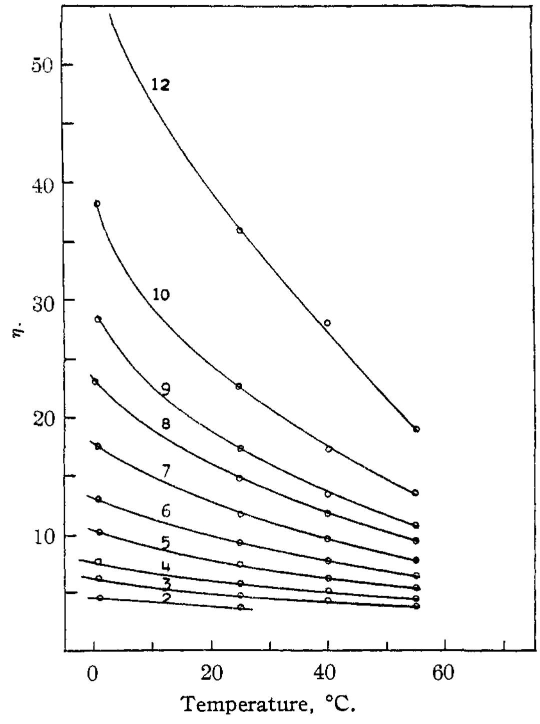

Fig. 9.—Dependence of viscosity (millipoises) of the normal alkyl bromides upon temperature. The number on each curve is the number of carbon atoms in the molecule.

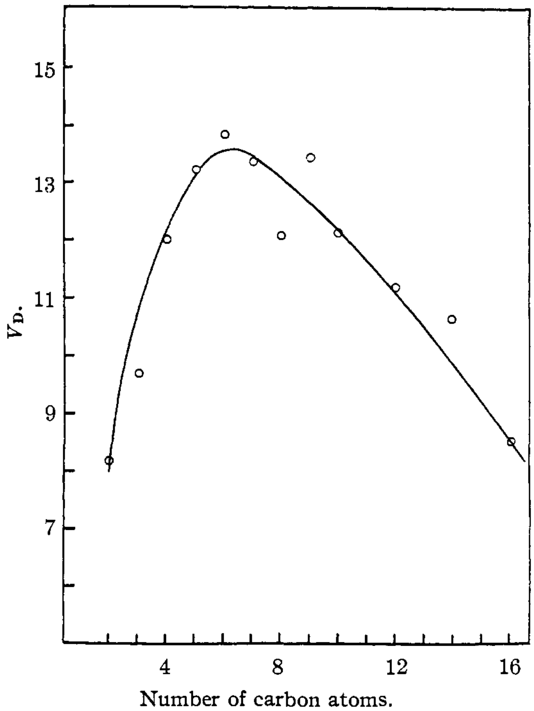

Fig. 10.—Dependence of V_D at 25° upon chain length.

measured molar volumes, V, to be reported in another paper shows a similar relation between the two quantities with the ratio decreasing for the long chain molecules to less than 0.03 for hexadecyl bromide. If the liquid were a system of close-packed molecular spheres, the ratio of the actual volume of the spheres to the total volume of the liquid would be 0.74. In Fig. 10 the values of V_D for the straight-chain alkyl bromides rise to a maximum for the six carbon chain instead of showing a continuous increase with increasing number of carbon atoms as would be the case if the values of V_D represented true volume. Although the critical wave lengths and relaxation times increase with increasing chain length for all the straight-chain molecules investigated, it appears that the previously mentioned increasing internal orienting power of the molecular chains causes their increase with increasing chain length to fall farther and farther behind the increase in viscosity.

TABLE II

VALUES OF $V_D = \tau_0 RT/3\eta$ AT 25°

Ethyl bromide	8.19	*n*-Tetradecyl bromide	10.68
n-Propyl bromide	9.67	*n*-Hexadecyl bromide	8.55
i-Propyl bromide	9.41	*n*-Octyl chloride	12.28
n-Butyl bromide	12.03	*n*-Octyl iodide	16.30
i-Butyl bromide	11.23	*n*-Dodecyl chloride	9.82
s-Butyl bromide	10.52	Cyclohexyl bromide	8.05
t-Butyl bromide	6.83	Chlorobenzene	11.25
n-Amyl bromide	13.23	Bromobenzene	12.54
n-Hexyl bromide	13.84	α-Chloronaphthalene	13.79
n-Heptyl bromide	13.37	α-Bromonaphthalene	15.72
n-Octyl bromide	12.08	Ethylene chloride	7.32
n-Nonyl bromide	13.45	Ethylene bromide	5.99
n-Decyl bromide	12.15	Tetramethylene chloride	5.94
n-Dodecyl bromide	11.21		

As was observed previously,[15] branching of the chain in the shorter molecules shortens the critical wave length. Thus, at 25° the critical wave length for *i*-propyl bromide is 0.1 cm. shorter than that for *n*-propyl bromide, and for the butyl bromides the values decrease from 1.64 for the normal compound to 1.56 for the iso, 1.34 for the secondary and 1.17 for the tertiary. The values of V_D also decrease. This decrease in the critical wave length which indicates an increase in the ease of orientation with change in molecular shape from that of a rod toward that of a sphere is not accompanied by a consistent decrease in the viscosity of the liquid. It would appear that while molecular orientation, which occurs merely through rotation, is facilitated by approach toward sphericity, translational motion, which is required for viscous flow in addition to rotation, may be hindered by the increase in the smallest molecular dimension caused by branching of the chain.

Ring formation increases the values found for the critical wave length and greatly increases the viscosity. At 25°, the critical wave length of *n*-hexyl bromide is 2.96 cm., that of bromobenzene is 3.09, and that of cyclohexyl bromide is 3.67. The difference between the critical wave length at 25° of *n*-decyl bromide, 6.32 cm., and that of α-bromonaphthalene, 16.20, is relatively greater than the difference in viscosities, in accordance with the increased opportunity for intramolecular orientation in the long straight-chain molecule in contrast to the rigidity of the α-bromonaphthalene molecule.

In Table III are assembled the values of the critical wave lengths, the viscosities, the molar volumes and the molar refractions at 25° for several sets of analogous molecules, the formulas of which are given in the first column.

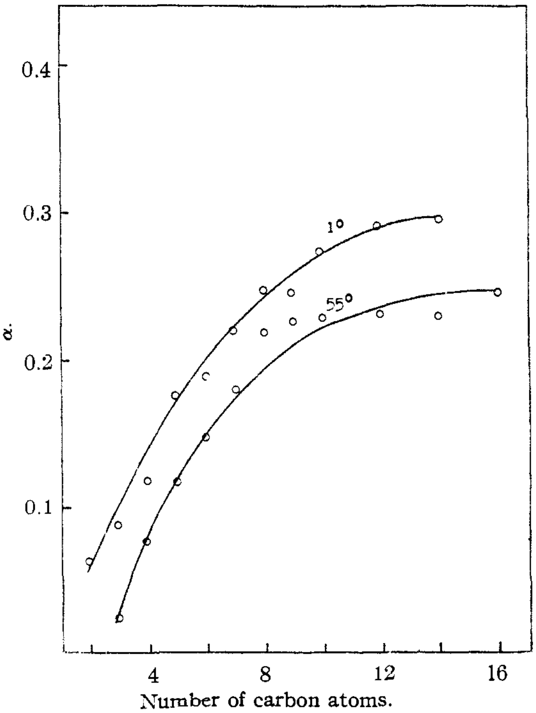

Fig. 11.—Dependence of α upon chain length.

TABLE III

CRITICAL WAVE LENGTHS, VISCOSITIES, AND MOLAR VOLUMES AND REFRACTIONS OF ANALOGOUS HALIDES AT 25°

	λ_m(cm.)	$\eta(\times 10^3)$	V(cc.)	R_D
$CH_3CH_2CH_2Br$	1.09	4.95	91.61	23.72
$BrCH_2CH_2Br$	2.18	16.00	86.58	27.01
$ClCH_2CH_2Cl$	1.31	7.90	79.46	21.07
n-$C_8H_{17}Cl$	3.22	11.50	170.78	44.03
n-$C_8H_{17}Br$	4.09	14.90	174.37	46.94
n-$C_8H_{17}I$	7.24	19.50	181.37	51.97
n-$C_{12}H_{25}Cl$	5.92	26.50	237.18	62.72
n-$C_{12}H_{25}Br$	9.20	36.00	241.04	65.57
C_6H_5Cl	1.94	7.56	102.24	31.20
C_6H_5Br	3.09	10.80	105.50	34.00
α-$C_{10}H_7Cl$	9.24	29.40	138.88	49.49
α-$C_{10}H_7Br$	16.2	45.20	140.02	51.46

It is apparent that, although the molar volumes of the bromides and also the molar refractions in Table III are only a little larger than those of the corresponding chlorides, while the dipole moments are known to be almost identical, the viscosities and hence the critical wave lengths are much larger. The increase in the polarizability of the halogen atom with consequent increase in the van der Waals attractive forces between the molecules may account for the increase in viscosity and critical wave length from octyl chloride to bromide to iodide as well as the increases from other chlorides to bromides. Similarly, the greater polarizability of the bromine atom as compared to the methyl group may account for the increase in viscosity and critical wave length from *n*-propyl bromide to ethylene bromide.

Distribution of Relaxation Times

The value of the empirical quantity α gives an approximate indication of the extent of the distribution of relaxation times for a molecule. The values in Table IV decrease with rising temperature showing an increase in uniformity of the potential barriers hindering molecular orientation throughout the liquid. The curves in Fig. 11 for the dependence of α for the straight-chain alkyl bromides upon the number of carbon atoms in the chain show a rapid rise from a small value for the ethyl bromide molecule with a flattening-out at 1° in the vicinity of a fourteen-carbon chain and a flattening at 55° in the vicinity of a ten-carbon chain. The increase in α with increase in chain length could be attributed to increase in the number of shapes which the molecules can acquire by twisting around the carbon–carbon bonds. Although this increase in the variety of molecular shapes may contribute somewhat to the increase, it does not account for the flattening out of the curve for the longer chains. If, as the number of bonds increases, dipole orientation occurs to an increasing extent by twisting around the bonds of the molecule instead of by orientation of the molecule as a whole, the maximum rotating unit may rarely exceed the segment of chain extending ten to twelve carbon atoms from the dipole, in which case α would increase little, if at all, with increase in the chain beyond the length of this segment.

TABLE IV

VALUES OF α AT DIFFERENT TEMPERATURES

	1.0°C.	25.0°C.	55°C.
Ethyl bromide	0.064	0.055	...
n-Propyl bromide	.087	.087	0.033
i-Propyl bromide	.031	.009	.000
n-Butyl bromide	.119	.098	.078
i-Butyl bromide	.035	.032	.000
s-Butyl bromide	.000	.000	.000
t-Butyl bromide	.040	.032	.000
n-Amyl bromide	.177	.143	.118
n-Hexyl bromide	.189	.172	.148
n-Heptyl bromide	.220	.204	.180
n-Octyl bromide	.248	.226	.220
n-Nonyl bromide	.246	.243	.227
n-Decyl bromide	.273	.251	.229
n-Dodecyl bromide	.293	.259	.232
n-Tetradecyl bromide	.299	.270	.235
n-Hexadecyl bromide	...	.287	.248
n-Octyl chloride	.224	.206	.180
n-Octyl iodide	.204	.197	.191
n-Dodecyl chloride	.260	.247	.188
Cyclohexyl bromide	.177	.108	.073
Chlorobenzene	.100	.048	.018
Bromobenzene	.110	.097	.069
α-Chloronaphthalene	.182	.084	.069
α-Bromonaphthalene	...	.161	.103
Ethylene chloride	.052	.041	.000
Ethylene bromide	...	.075	.033
Tetramethylene chloride	.091	.082	.000

Branching of the chain in the propyl and butyl bromides lowers α so that in *s*-butyl bromide and *t*-butyl bromide, the molecule of which is almost spherical, it is indistinguishable from zero. The cyclic molecules have lower values of α than the straight chain molecules containing the same number of carbon atoms since they possess less variety of modes of orientation.

The decrease in the distribution of relaxation times with rising temperature causes a number of somewhat unsymmetrical molecules to conform fairly well to the Debye equations at 55°. It seems probable that the nearer approach to random molecular orientation brought about by rising temperature may account for the reduction in the distribution of the relaxation times.

Application of Absolute Rate Theory

Dielectric loss may be discussed in terms of the absolute rate theory[15] by treating dielectric relaxation as a rate process in which the polar molecules rotate from one equilibrium position to another. This process of rotation requires an activation energy sufficient to overcome the energy barrier separating the two mean equilibrium positions. The number of times such a rotation will occur per second is given by the familiar rate expression

$$K = \frac{1}{\tau_0} = \frac{kT}{h}\, e^{-\Delta F_{\epsilon}^{\mp}/RT} \qquad (21)$$

where $\Delta F^{\mp}_{\epsilon}$ is the free energy of activation for dipole relaxation. Since $\Delta F = \Delta H - T\Delta S$, the equation may be rewritten

$$\tau_0 = \frac{h}{kT}\, e^{\Delta H^{\mp}_{\epsilon}/RT} e^{-\Delta S^{\mp}_{\epsilon}/R} \qquad (22)$$

where $\Delta H^{\mp}_{\epsilon}$ is the heat of activation for dipole relaxation and $\Delta S^{\pm}_{\epsilon}$ is the entropy of activation for dipole relaxation. $\Delta S^{\mp}_{\epsilon}$ may be calculated since $\Delta F^{\mp}_{\epsilon}$ is now known and $\Delta H^{\mp}_{\epsilon}$ is obtained from the slope of the curve for $\ln \tau_0$ plotted against $1/T$, since differentiation of equation (22) gives

$$\Delta H^{\mp}_{\epsilon} = (R\, \mathrm{d} \ln \tau_0/\mathrm{d}(1/T)) - RT \qquad (23)$$

The viscosity of liquids may be approached in an analogous manner. Viscous flow is pictured as the movement of one layer of molecules with respect to another layer, involving translational as well as rotational motion of the molecules, with an activation energy required to pass over a hindering potential energy barrier. The equation derived for the viscosity in terms of this mechanism is

$$\eta = \frac{hN}{V}\, e^{\Delta F^{\mp}_{\mathrm{v}}/RT} \qquad (24)$$

where $\Delta F^{\mp}_{\mathrm{v}}$ is the free energy of activation for viscous flow, and V is the molar volume. ΔF_{v}, as before, may be rewritten as $\Delta F_{\mathrm{v}} = \Delta H_{\mathrm{v}} - T\Delta S_{\mathrm{v}}$, or

$$\eta = \frac{hN}{V} e^{\Delta H^{\mp}_{\mathrm{v}}/RT} e^{-\Delta S^{\mp}_{\mathrm{v}}/R} \qquad (25)$$

Multiplication of equation (22) by equation (25) gives[15]

$$\eta V/\tau_0 RT = e^{(\Delta F^{\mp}_{\mathrm{v}} - \Delta F^{\mp}_{\mathrm{v}})/RT} \qquad (26)$$

an expression which is useful in comparing the processes of dipole rotation and viscous flow.

The temperature dependence of the relaxation time, τ_0, which is proportional to the critical wave length is used, according to equation (23), to calculate the values of the heat change of activation for dielectric relaxation, $\Delta H^{\mp}_{\epsilon}$, from the slopes of the straight lines obtained by plotting the logarithm of the relaxation time, τ_0, against the reciprocal of the absolute temperature (Fig. 12). Similarly, the values of the heat change of activation for viscous flow, $\Delta H^{\mp}_{\mathrm{v}}$, are obtained approximately from the slopes of the curves for the logarithms of the viscosities against the reciprocals of the absolute temperatures (Fig. 13). The values of the free energy of activation for dielectric relaxation, $\Delta F^{\mp}_{\epsilon}$, are calculated at three temperatures by means of equation (21) and those of the free energy of activation for viscous flow, $\Delta F^{\mp}_{\mathrm{v}}$, are similarly calculated by means of equation (24). The

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

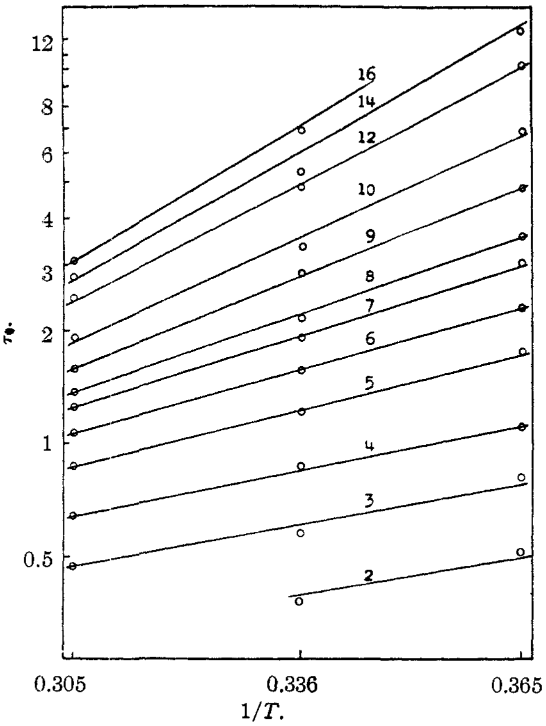

Fig. 12.—Dependence of the logarithm of τ_0 (1×10^{11}) in sec. upon the reciprocal of the absolute temperature (1×10^2). The number on each curve is the number of carbon atoms in the molecule.

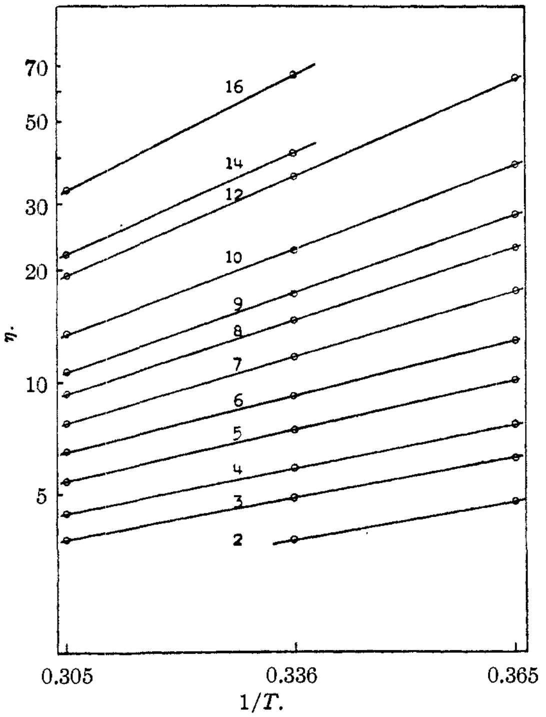

Fig. 13.—Dependence of the logarithm of η (millipoises) upon the reciprocal of the absolute temperature (1×10^2). The number on each curve is the number of carbon atoms in the molecule.

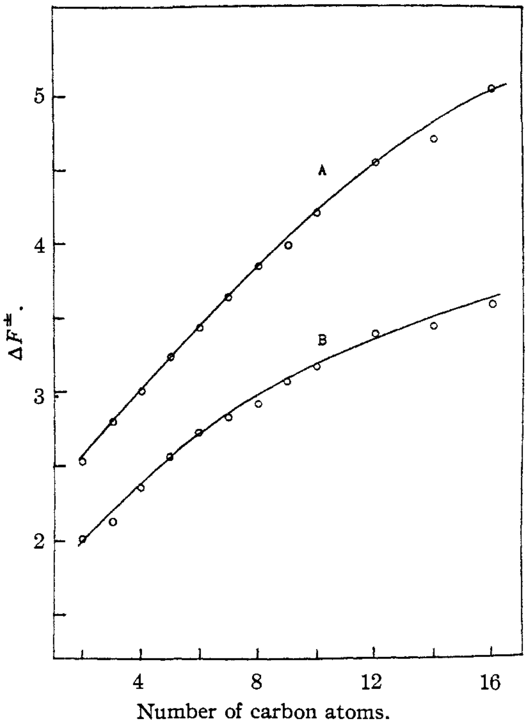

Fig. 14.—Dependence of free energies of activation (kcal./mole) upon chain length: (A) viscous flow, (B) dielectric relaxation.

entropies of activation for the two processes follow directly from these values.

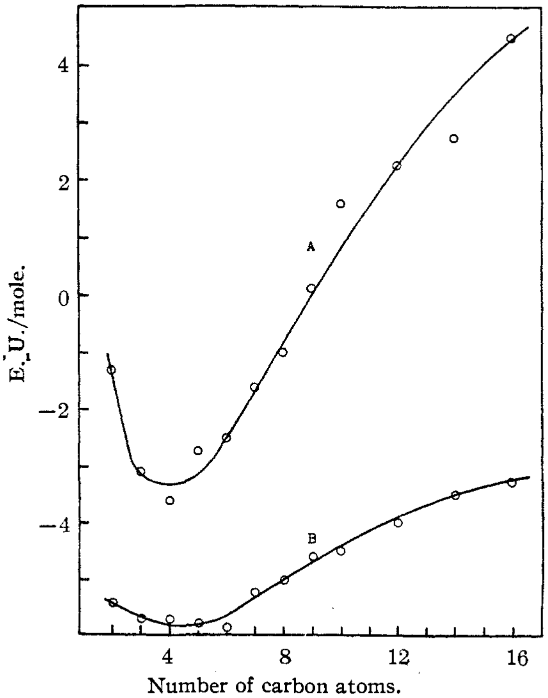

Fig. 15.—Dependence of $\Delta S^{\neq}$ for dielectric relaxation (A) and viscous flow (B) upon chain length.

In Fig. 14 the curve for the free energy change of activation for dielectric relaxation at 25° plotted against the number of carbon atoms in the molecular chain is rather similar in form but somewhat lower than the corresponding curve for viscous flow. The ratio $\Delta F_\epsilon / \Delta F_V$ remains close to 0.6 over the range from two to sixteen carbon atoms. An analogous difference between ΔF_ϵ and ΔF_V was noted in earlier work[15] and attributed to the fact that dielectric relaxation primarily requires only molecular rotation, while viscous flow requires translation in addition to rotation. Both curves show some tendency to level off, which could arise from increased internal rotation with increasing chain length. In Fig. 15 the curves for the entropies of activation at 25° for the two processes are similar in shape, but the values for viscous flow are all negative, while in the case of dielectric relaxation the values are negative for the smaller molecules and positive for the larger.

Conclusions

The dielectric behavior of four of the twenty-seven polar liquids which have been investigated in the course of the present work over a 54° range of temperature conforms closely to that required by the Debye theory of anomalous dielectric dispersion with a single relaxation time. The shapes of these four molecules, *i*-propyl, *i*-butyl, *s*-butyl and *t*-butyl bromide, are not far from the spherical form postulated in the derivation of the Debye equations. It is only for these nearly spherical molecules that one might expect close conformity to the Debye equations. Increasing molecular chain length gives increasing departure from the Debye equations and requires an increasing width in the distribution of relaxation times. Rising temperature reduces the distribution of relaxation times so that a number of moderately unsymmetrical molecules conform fairly well to the Debye equations at 55°.

The increase in the distribution of the relaxation times with increasing molecular chain length could arise from increase in the variety of molecular shapes caused by twisting around the carbon–carbon bonds. It appears probable, however, that a major cause of the distribution lies in the orientation of the molecular dipole through twisting around these bonds.

The very close parallelism between critical wave length or dielectric relaxation time and viscosity in dependence upon molecular size and temperature gives further evidence of the previously observed similarity between the processes of dielectric relaxation and viscous flow. This similarity is further emphasized in the behavior of the activation energies, free energies and entropies of the two processes.

Summary

The dielectric constants and loss factors of twenty-seven liquid organic halides measured at 1.27 and 3.22 cm. wave length and published in the first two papers of this series are used together with viscosities, densities and refractive indices to study the accuracy of the Debye equations for dielectric behavior and the empirical modification proposed by Cole and Cole. The loss factors are satisfactorily represented by the semi-circular arc plots of Cole and Cole, which are used to calculate values for the critical wave length, the wave length at which the loss factor has its maximum value, and the corresponding relaxation time.

Of the twenty-seven polar molecules having different sizes, shapes and rigidities, those which are approximately spherical in shape conform closely to the Debye theory of dielectric relaxation which assumes spherical molecules. A distribution of relaxation times is found for the unsymmetrical molecules, increasing with molecular asymmetry and decreasing with rising temperature. This distribution may arise from the existence of the longer molecules in a variety of shapes caused by twisting around the carbon–carbon bonds as well as from orientation of the molecular dipole by twisting around these bonds.

Curves for critical wave lengths and for viscosities plotted against number of carbon atoms in the molecular chain and against temperature show close parallelism between the processes of dielectric relaxation and viscous flow. The activation energies calculated for the two processes give further evidence of this similarity.

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