of this relationship appears to be independent of molecular weight. Reliable methods for extrapolating π/c to $c = 0$ have been established, enabling the determination of absolute molecular weights with satisfactory precision up to values of about 1,000,000.

Molecular weights of polyisobutylenes calculated from Staudinger's equation are too low; the discrepancy is more than ten-fold at high molecular weights.

On the basis of data for carefully fractionated samples covering a two-hundred-fold molecular weight range, the intrinsic viscosity is found to be proportional to the 0.64 power of the molecular weight. This decided deviation from Staudinger's "law" cannot in this instance be attributed to non-linear chain structure, as Staudinger has sought to do in other cases.

This dependence of molecular weight on intrinsic viscosity leads to the definition of a "viscosity average" molecular weight which is obtained when the relationship is applied to heterogeneous polymers. The viscosity average is less than the weight average molecular weight, which would be obtained if Staudinger's equation were applicable, and greater than the number average obtained by osmotic or cryoscopic methods.

ELIZABETH, N. J. RECEIVED NOVEMBER 18, 1942

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dielectric Dispersion and Absorption of Water and Some Organic Liquids

BY W. P. CONNER[1] AND C. P. SMYTH

The measurement of dielectric constants and the related loss factor of polar liquids at very high radio frequencies has long been a subject of investigation. Within recent years the improved experimental accuracy has made possible the determination of molecular size and shape, and of the potential barrier involved in dipole rotation from these data. This report records measurements carried out at 3.08×10^9 cycles with water from 0 to 100° and with sixteen organic compounds at 25°. The results are analyzed with regard to the existing theories.

Although numerous values[2-8] of the relaxation time of water for room temperature are found in the literature, the temperature coefficient has not been determined. It is expected that a knowledge of the barrier height for this relaxation time will aid in the differentiation of the molecular mechanism between actual rotation of a definite dipole and merely the jumping of a hydrogen atom from an equilibrium position near one oxygen atom to another equilibrium position near an adjacent oxygen atom.[9]

The Debye theory for the dispersion of the dielectric constant of polar liquids has been found unsatisfactory for relating the frictional torque opposing molecular rotation to the macroscopic viscosity. The application[10] of the absolute reaction rate theory to the rotational process indicates that its mechanism is very similar to that involved in viscous flow. This viewpoint is further discussed in the present paper.

Experimental

Materials.—The water used in this investigation was distilled in the usual way. Careful washing of the cell kept the direct current salt conductivity as low as possible. At the high frequency at which measurements were made, 3.08×10^9 cycles per second, both the elevation of the dielectric constant resulting from the Debye–Hückel effect and the increase in the loss factor from salt conductance are negligible. The organic compounds used had been previously carefully purified for low frequency dielectric constant measurements in this Laboratory. However, since they had been standing for some time in tightly stoppered bottles in the dark, small amounts of water may have been present and also slight decomposition may have occurred in the most unstable compounds.

Apparatus.—The frequency source will be discussed in a future publication. Suffice it to say that it was completely stable in its wave length (9.72 cm.) and power output except for sudden momentary thermal fluctuations. The dielectric constants were determined by measurement of the wave length of standing waves in coaxial tubes filled with the liquid to be investigated, the dielectric constant being

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(1) Research Assistant on special funds from the Rockefeller Foundation.

(2) Tear, *Phys. Rev.*, **21**, 611 (1923).

(3) Ardenne, Groos and Otterbein, *Physik. Z.*, **37**, 535 (1936).

(4) Schmelzer, *Ann. Physik.*, **28**, 35 (1937).

(5) Hackel and Wien, *Physik. Z.*, **38**, 767 (1937).

(6) Bäz, *ibid.*, **38**, 774 (1937); **40**, 394 (1939).

(7) Slevogt, *Ann. Physik*, **36**, 141 (1939).

(8) Kebbel, *Z. Hochfr.*, **53**, 81 (1939).

(9) Bernal and Fowler, *J. Chem. Phys.*, 1, 515 (1933); Pauling, "The Nature of the Chemical Bond," 2d ed., Cornell University Press, Ithaca, N. Y., 1940, p. 302.

(10) Powell and Eyring, "Advances in Colloid Science," Vol. I, edited by Kraemer, Interscience Publishers, Inc., New York, N. Y., 1942.

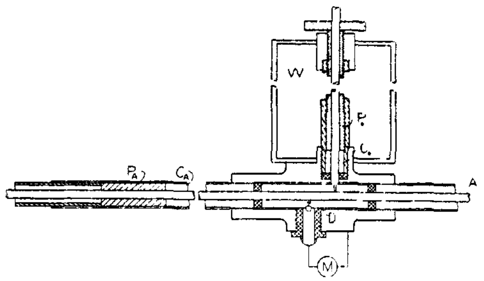

Fig. 1.—Concentric line receiver for high frequency dielectric constant measurements: C_A, resonance circuit in air; C_L, resonance circuit in liquid; P_A, P_L, plungers; D, crystal detector; M, microammeter; A, connection to attenuator; W, water-jacket; cross-hatching, leucite or bakelite.

equal to the square of the ratio of the wave length in air to that in the liquid in question. The method was similar to that reported previously,[11] except for minor changes in tube dimensions and methods of detection necessitated by the much higher frequency. A schematic description of the receiving apparatus is given in Fig. 1. The outer tube diameter was one-quarter inch for both resonance chambers, C_A and C_L. For the air determinations the inner tube was one-sixteenth inch in diameter, and for the polar liquids one-eighth inch. It would have been desirable to reduce the size of both tubes for the liquids, but constructional difficulties made the most desirable[12] tube sizes impossible. Tube lengths were 30 cm. for the air and 12 cm. for the liquid chamber. Brass was used for all metal surfaces not in contact with liquid, while stainless steel was used for all conducting surfaces likely to be corroded by contact with liquid. For the lower temperatures leucite was used for insulation. However, because of the tendency of this plastic to flow, at elevated temperatures, 70° to 100°, bakelite was substituted. At 100° it was necessary to add a lead washer seal to prevent leakage of water. Both plungers, P_A and P_L, were attached to micrometer screws which were threaded to 40 and 20 turns per inch for the liquid and air chambers, respectively. The galena crystal D was given to us by Dr. S. O. Morgan of the Bell Telephone Laboratories. The Rawson multimeter M, which was used to measure the current, had a full scale deflection from 0.1 to 1000 milliamperes in decade steps. A shunt was incorporated in the circuit so that the meter could be set to any desired initial reading.

Since it was not possible to vary the coupling to the oscillator, it was necessary to insert in the circuit an attenuator so that the variation in the load impedance of the receiver did not change the frequency of the oscillator. The attenuator used was a simple air resonance circuit like that in Fig. 1 with the water resonance circuit removed. Coupling was varied by changing the length of the internal tube of the coupling line which extended into this resonance air chamber at right angles. Coupling was considered sufficiently loose, when a slight increase in coupling produced no measurable change in the position of the plunger in the air chamber for maximum current in the microammeter. Actually, because of the power output and stability of the oscillator, this coupling was not at all critical. Maximum microammeter current could be used up to 10 milliamperes.

The wave form in the air chamber, as determined by recording the microammeter reading as the air plunger (the water plunger remaining fixed) is moved by steps of 0.025 inch away from the input end of the chamber, is shown by curve A in Fig. 2. This diagram is only one-half a total wave length, equivalent points between two adjacent diagrams being 1.917 inches apart. Since the oscillator gave a very good sine wave, low in harmonics, the deviation of this wave form from a sine curve is to be found in the arrangement of the coaxial tube system. Standard theory of transmission lines[13] indicates that this is the predicted result for a transmission line of output reflection coefficient equal to unity in which there is very slight absorption and for which the input reflection coefficient is not quite unity if the point of detection, the crystal, is held arbitrarily fixed. Because of the need for mechanical rigidity it was not feasible to install in the detector a crystal which might be moved along the transmission lines.

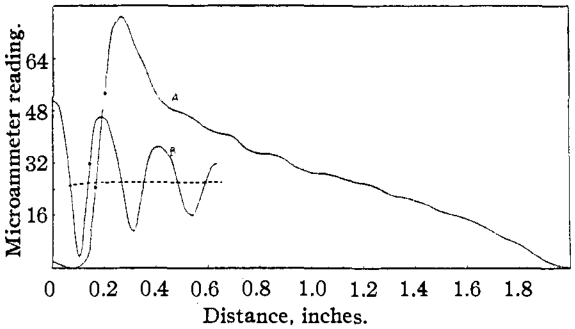

Fig. 2.—Wave form in (A) air and (B) water.

The wave form in the liquid chamber is shown by curve B in Fig. 2 for distilled water at 25°. For this determination the plunger in the air column was adjusted to maximum microammeter current, and then the plunger in the water chamber was withdrawn from its initial position at the base of the cell in steps of 0.010 inch. The more nearly sine wave nature of the curve in water as compared to the curve in air is due to the reduction of the number of multiple reflections within the liquid column because of the much higher absorption coefficient in water. However, the mean line drawn horizontally is not a straight line, but starts rather low and approaches the horizontal slowly. If the input reflection coefficient of the water column had been exactly zero, the mean line would have been straight. The position of each maximum and minimum was determined by drawing a vertical mean line through the peak or trough until it intersected the experimental curve. The distance between two similar points was taken as one-half the wave length in the medium.

In addition to the dielectric constant, the loss factor of the liquids was determined from the attenuation of the waves in the liquid chamber. Transmission line theory indicates that, for a low input reflection coefficient in a shorted line, a

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(11) Conner and Smyth, THIS JOURNAL, **64**, 1870 (1942).

(12) Reukema, *Elec. Eng.*, **56**, 1002 (1937).

(13) *Cf.* Page and Adams, "Principles of Electricity," D. Van Nostrand Co., Inc., New York, N. Y., 1931, p. 540.

curve like B of Fig. 2 would be such that, in close approximation, alternate maxima or minima as measured from the straight horizontal line would be in the ratio of $e^{\alpha\lambda}$, where α is the attenuation constant per unit length of line and λ is the wave length in the medium. By the transformation

$$\epsilon'' = \alpha\lambda\epsilon/\pi$$

in which ϵ is the dielectric constant, ϵ'', the imaginary component, may be determined.

When the liquid column length is short, the absorption of the electric wave is not sufficient to prevent the wave reflected at the input plane, after having traveled the length of the liquid column and back, from still being very effective in determining the electric intensity at the detector. Thus only for rather long liquid columns, is the mean horizontal line completely straight. However, the ratio of these initial maxima measured from the curved horizontal line is not greatly different from those measured for longer liquid column lengths.

For high dielectric constants and low loss factors the number of maxima and minima is greatest. Such a condition holds most closely for water at higher temperatures. Thus in Table I are recorded the ratios of alternate maxima and of alternate minima for distilled water at 90°. As one progresses down the table, determinations become more inaccurate since the variation between maximum and minimum is becoming less.

TABLE I

$e^{\alpha\lambda}$ FOR WATER AT 90°

Ratio of maxima	Ratio of minima
1.203	1.248
1.222	1.258
1.265	1.258
1.257	1.248
1.222	1.228
1.250	1.208
1.217	1.230
1.238	
Av. 1.234	Av. 1.239

To complete the calculation of ϵ'', since ϵ is 57.7

$$\epsilon'' = \frac{2.3 \log_{10} 1.234}{\pi}\,\epsilon = 3.95$$

The determination of the dielectric constant as the square of the ratio of the wave length in air to that in the liquid is in error if the absorption is large, as was discussed by Drake, Pierce and Dow.[14] In view of the large values of ϵ'' for the lower temperatures, it was thought that there might be an appreciable error in the determination of the dielectric constant from the square of the ratio of wave lengths. Use was made of the approximate equation given by Drake, Pierce and Dow[14]

$$\epsilon = \frac{n^2}{(1 - \eta h)\,f^2(h)}$$

where n is the ratio of wave length; η is a constant of the apparatus, proportional to the total resistance of the coaxial tubes, and is much less than unity for the apparatus as the equation requires; h, in this approximation, is equal to ϵ''/ϵ, and $f(h)$ is a function given in the original paper. In Table II are recorded the calculated corrections.

TABLE II

t, °C.	ϵ''/ϵ	$f(h)$	$1/f^2(h)$	$\epsilon_{\text{cor.}}$	$\epsilon_{\text{uncor.}}$
0	0.310	1.0116	0.977	78.2	80.0
14	.221	1.0058	.988	78.0	79.0
25	.1800	1.0040	.992	76.5	77.1
50	.1208	1.0020	.996	69.3	69.5
75	.0835	1.0010	.998	63.4	63.5

It is seen that only at 0° are these corrections greater than the error of the dielectric constant determination, while above 75° they are undetectable. In view of the smallness of the error, the uncorrected values were used for the calculation of relaxation times.

Measurements were less accurate with highly absorbing liquids since the minima and maxima were smaller in magnitude and more rapidly damped out. Also, because of the physical shortness of the liquid column used, fewer maxima could be obtained with liquids of lower dielectric constant, and, consequently, the accuracy was somewhat reduced. In general, ϵ was determined within ±1% and ϵ'' within ±2%. Since ϵ occurs in both numerator and denominator of the equation from which λ_c is calculated, a 20% variation in ϵ for water will still leave λ_c unchanged within 1%.

Results.—In Table III are recorded the values of ϵ and ϵ'' of water at 9.72 cm. wave length for a temperature range of 0 to 100°. Included also are the values of the static dielectric constant ϵ_0, calculated from the equation given by Drake, Pierce and Dow,[14]

$$\epsilon_t = 78.57\ [1 - 0.00461\ (t - 25) + 0.0000155\ (t - 25)^2]$$

and, at 0 and 100°, from the measurements of Wyman.[15]

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(14) Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930).

(15) Wyman, *Phys. Rev.*, **35**, 623 (1930).

TABLE III

DIELECTRIC DATA FOR WATER

t, °C.	ϵ (9.72 cm.)	ϵ'' (9.72 cm.)	ϵ_0	λ_c, cm.	$\tau \times 10^{12}$ sec.	q	$\tau' \times 10^{12}$ sec ^{1}
0	80.0	24.8	88.01	3.12	16.5	0.926	8.75
14	79.0	17.42	82.70	2.22	11.87	.920	6.18
25	77.1	13.88	78.57	1.81	9.58	.915	4.89
50	69.5	8.39	70.28	1.21	6.40	.912	3.39
75	63.5	5.30	63.51	0.845	4.46	.912	2.50
80	62.3	4.92	62.33	.800	4.24	.907	2.33
90	57.7	3.95	57.68	.695	3.68	.915	2.21
100	55.3	3.40	55.33	.625	3.31	.914	1.99

The critical wave length, λ_c, and the relaxation time, $\tau = \lambda_c/2\pi c$, c being the velocity of light, have been calculated from a modified Debye equation

$$\lambda_c = \frac{\epsilon''}{\epsilon - \epsilon_\infty}\lambda$$

in which λ is the measuring wave length, 9.72 cm. The equation has been obtained by dividing one of the Debye equations[16] by the other and setting the factor $(\epsilon_0 + 2)/(\epsilon_\infty + 2)$ equal to unity, as is indicated by both the Wyman empirical investigation and the Onsager[17] theory of the dielectric constants of polar liquids. ϵ_∞, the dielectric constant at frequencies so high that orientation of the polar molecules does not contribute to it, was taken as 2.5, a value appreciably higher than the square of the refractive index, because the data of Tear[2] for very short waves and the dielectric constant found in this Laboratory for ice at low temperature indicated a large atomic polarization. Actually, because of the magnitude of ϵ, a variation of 20% in ϵ_∞ affected the value calculated for λ_c by less than 1%. At 25°, the value of λ_c, 1.81, is in close agreement with the best literature[6,7,8] value, 1.85. Other values previously reported are 1.2–1.7,[4] and 1.80.[5]

The quantity λ_c may be calculated from ϵ by the Debye equation[16] written in the form

$$\lambda_c = \lambda\left(\frac{\epsilon_0 - \epsilon_\infty}{\epsilon' - \epsilon_\infty} - 1\right)^{1/2}$$

in which ϵ at 9.72 cm. is taken as ϵ' and the factor $(\epsilon_0 + 2)/(\epsilon_\infty + 2)$ is again taken as 1. At 0°, the data in Table III give 3.13 cm. for λ_c and, at 14°, 2.22, in better agreement with the values obtained from the absorption than is warranted by the precision of the data. Above 14°, the differences between ϵ_0 and ϵ at 9.72 cm. are too small to give the calculation any significance.

The seventh column in Table III gives the values calculated for an empirical correction factor q introduced by Cole,[18] and the last column gives relaxation time values, τ', calculated by the equation into which this correction factor q was introduced.[18] Because of the subtractions involved, the relative errors in the corrected values are larger. The values themselves are smaller than those for the uncorrected τ since the use of q reduces them toward the much smaller values which would be obtained by the use of the Debye equation unmodified by the assumption that $(\epsilon_0 + 2)/(\epsilon_\infty + 2) = 1$.

Throughout this discussion it has been assumed that, for water, only one relaxation time is involved and the dispersion of the dielectric constant thus occurs over approximately two logarithmic units of frequency. The facts that the dispersion does not set in until such high frequency is reached and that the calculated relaxation times are of about the right order of magnitude lend weight to this argument. Moreover, the data of Tear[2] taken over the high frequency end of the dispersion region can be well represented by a single relaxation time if the absorption bands are ignored. Plotting ϵ'' against ϵ', as was suggested by Cole and Cole,[19] for the three points whose abscissas are given by $\epsilon' = \epsilon_\infty$, $\epsilon_{9.72}$, and ϵ_0 at the lowest temperatures where the test is more critical, shows that, at each temperature, these three points lie closely upon a semicircle whose center is on the ϵ' abscissa in Fig. 3. Deviation of the centers of these semicircles from the line of the abscissa would indicate more than one relaxation time. Although it is not possible to draw a definite conclusion from three points alone, it is indicated that only a single τ value is involved.

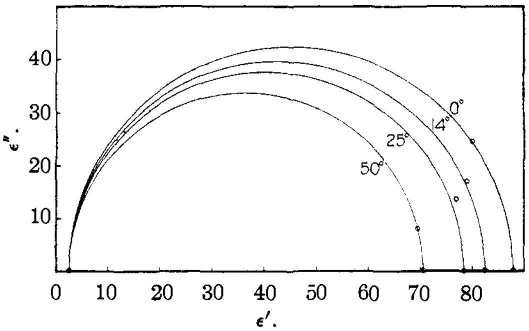

Fig. 3.—Semicircular plot of complex dielectric constants of water.

The logarithm of the relaxation time τ is plotted in Fig. 4 against the reciprocal of the absolute

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[16] Debye, "Polar Molecules," The Chemical Catalog Co., Inc., New York, N. Y., 1929, p. 97.

[17] Wyman, THIS JOURNAL, **58**, 1482 (1936); Onsager, *ibid.*, **58**, 1486 (1936).

[18] Cole, *J. Chem. Phys.*, **6**, 385 (1938).

[19] Cole and Cole, *ibid.*, **9**, 341 (1941).

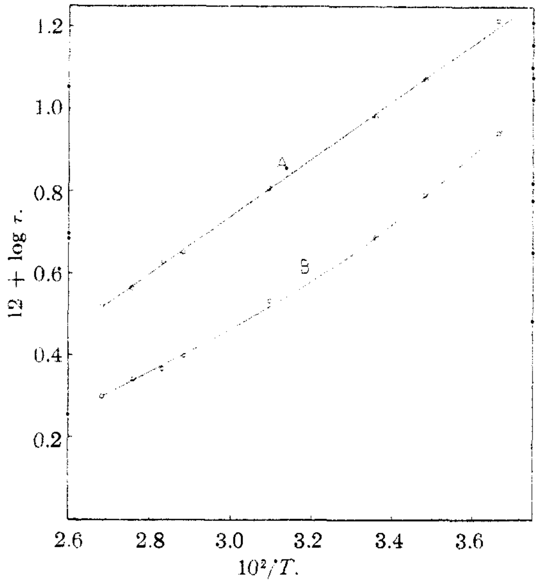

Fig. 4.—Dependence of the logarithm of the relaxation time of water—A, uncorrected; B, corrected—upon the reciprocal of the absolute temperature.

temperature as curve A, which appears to be linear. Eyring,[20] considering dipole relaxation time from the viewpoint of the absolute reaction rate theory as the reciprocal of a rate of passage of the molecule over a potential barrier, writes

$$\tau = (h/kT)e^{\Delta F^{\ddagger}/RT} = (h/kT)e^{(\Delta H^{\ddagger} - T\Delta S^{\ddagger})/RT}$$

where $\Delta F^{\ddagger}$ is the free energy of activation for a single rotation and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the corresponding heat and entropy of activation. Since it follows that $\Delta H^{\ddagger} = R \text{ d} \log \tau/\text{d}(1/T) - RT$, $\Delta H^{\ddagger}$ may be found from the slope of curve A in Fig. 4. The thermodynamic values calculated by means of these equations are recorded in Table IV, as are also the analogous quantities for viscous flow according to Eyring's theory.

TABLE IV

$\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$ AND $\Delta S^{\ddagger}$ FOR ROTATION IN WATER

	Dipole			Viscosity		
t, °C.	$\Delta F^{\ddagger}$, kcal.	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e. u.	$\Delta F^{\ddagger}$, kcal.	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e. u.
0	2.47	2.65	0.66	2.39	4.52	7.80
25	2.41	2.60	.63	2.21	3.47	4.23
100	2.40	2.45	.13	1.85	2.06	0.56
150				1.75	1.27	−1.13

For complete parallelism between the molecular mechanisms of dipole rotation and viscous flow, the entropy change for dipole rotation ought to show the same marked temperature dependence which is characteristic of viscous flow. Inasmuch as a more correct τ value for dipole rotation is obtained by the use of the empirical equation of Cole,[18] it is of interest to determine the entropy change with τ′ as the experimental quantity. In the plot of the log τ′ values against 1/T as shown by curve B in Fig. 4 an appreciable curvature is apparent so that $\Delta H^{\ddagger}$ must be determined from the slope at each temperature. The thermodynamic quantities calculated from these corrected values are given in Table V.

TABLE V

THERMODYNAMIC VALUES CALCULATED FROM τ′

t, °C.	$\Delta F^{\ddagger}$, kcal.	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e. u.
0	2.12	3.09	3.55
25	2.04	2.61	1.91
100	2.03	1.60	−1.15

Should the mechanism of rotation be largely that of proton transfer, it is reasonable to suppose that the activated state would be, at least, slightly restricted as compared to the initial state since, in the activated state, rotation of a single water molecule could not occur about an axis perpendicular to the direction of proton transfer. In fact, calculation of the entropy of the proton transfer process arising in the discussion[21] of the abnormal conductivity of water agrees well with this supposition, inasmuch as the heats of activation are found to be smaller than the free energies of activation. Thus, it appears that, as in normal polar organic compounds, the dipole polarization of water is the result of the rotation of individual dipoles with the electric field. This rate of dipole rotation agrees well with the assumption[21] that for conductance by proton transfer the actual proton transfer is slower than the rotation of the molecules largely because of the far fewer H_3^+O ions present in comparison to un-ionized water molecules.

It is interesting to note that in Table V the entropy for dipole rotation based on τ′ becomes negative at the higher temperatures. This negative entropy indicates that, although the molecules are rotating rather freely at this high temperature, they must still pass through a restricted state during the dipole rotation. Undoubtedly because of strong dipole interactions and hydrogen bonding, the molecules may pass over a lower temperature barrier if there is a degree of coöperation in their motions. Such a coöperative phenomenon probably involves relatively few molecules at these high temperatures. As this

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(20) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 548.

(21) Ref. 20, pp. 559–567.

negative entropy occurs also at the higher temperatures for viscous flow, a similar coöperative effect can be inferred. It is not thought that this negative entropy is the result of a proton transfer process for dipole rotation since, even at low temperatures, the entropy for proton transfer is already negative and is very much more negative at higher temperatures,[21] approximately -3.9 at 25° and -7.5 at 100°. Thus, the molecular process occurring in viscous flow appears to be quite adequate to explain dipole rotation. At low temperatures the majority of water molecules which have not acquired complete rotational freedom gain rotational entropy during the process of viscous flow or dipole rotation. As the temperature increases, the molecules rapidly gain rotational freedom. However, even at the higher temperatures the potential barrier for rotation is lower if the molecules coöperate somewhat in the rotational process. The greatly lowered potential barrier overshadows the decrease in entropy to such an extent that, for this process, the free energy is lowest, and, hence, this reaction is the rate determining process.

Obviously, in view of the approximations involved in the treatment, the precise numerical values of these thermodynamic quantities are not significant, but their order of magnitude and temperature dependence make it clear that the dipole polarization of water and, presumably, by analogy, that of other hydrogen bonded liquids, are due to rotational orientation of the molecules in the applied field and not to proton migration.

The polar compounds listed in Table VI were measured at 25° only. As they were, for the most part, old samples and were measured without repurification, the data in Table VI must be regarded merely as a preliminary survey of the field. Determinations of the viscosity η were carried out with an Ostwald viscosimeter with a time of flow of about one minute. Densities for the viscosity calculation were obtained from the literature, and, where the density at 25° was not given directly, a reasonable interpolation was made. The viscosities are probably accurate to about 2%. As in the case of water, the critical wave lengths were calculated by means of the simplified equation, in which only one relaxation time is assumed to be present. Since the ratio of ϵ'' to ϵ was, in general, less than 0.2, the correction to the dielectric constant due to absorption was neglected, for, as indicated in Table II, it was less than 1%. The value of the dielectric constant ϵ_∞ has been taken equal to the square of the refractive index, no correction being made for atomic polarization. The dielectric constant measured at 9.72 cm. for a pure sample of benzene, which, as expected, showed no dispersion or absorption, was indistinguishable from the value used in this Laboratory when the liquid is employed for calibration purposes. Although this evidences the precision of the measurements, it is unsafe, because of impurities in some of the samples as well as of variation of literature values, to draw any quantitative conclusions from the small dispersion shown by the liquids with the exception of octanol-1. The absorption is, however, highly significant.

Included in Table VI is the calculation of the molar volume, V_D, obtained from the Debye

TABLE VI

VISCOSITIES AND DIELECTRIC DATA FOR SOME ORGANIC COMPOUNDS AT 25°

Compound	η, millipoises	ϵ_∞	ϵ (9.72 cm.)	ϵ'' (9.72 cm.)	λ_c, cm.	$\tau \times 10^{12}$ sec.	V_D	V	$\eta V/\tau RT$
Benzene	6.08	2.25	2.28	0.0					
Chloroform	5.34	2.09	4.81	.379	1.36	7.18	11.58	80.2	2.46
Methylchloroform	7.95	2.07	7.02	.637	1.25	6.64	6.93	189	4.30
Ethyl iodide	5.50	2.28	7.76	.761	1.35	7.15	8.25	80.6	2.50
n-Butyl chloride	4.34	2.02	6.97	.745	1.46	7.75	14.8	106.2	2.40
t-Butyl chloride	4.86	1.92	9.7	.786	0.97	5.17	8.76	111	4.22
Trimethylene chloride		2.05	10.21	1.340	1.62	8.59			
s-Butyl bromide	5.91	2.06	8.73	1.300	1.78	9.44	13.2	108	2.73
i-Butyl bromide	6.03	2.06	6.98	0.880	1.74	9.23	21.4	108	2.84
n-Butyl iodide	8.43	2.20	6.01	1.346	3.32	17.62	17.3	115	2.21
i-Amyl chloride	5.00	2.00	6.07	0.730	1.74	9.23	15.3	128	2.79
t-Amyl chloride	4.37	1.99	6.95	.662	1.29	6.86	13.0	128	3.29
n-Amyl bromide	7.71	2.09	6.13	1.180	2.84	15.07	16.1	125	2.57
i-Amyl bromide	5.92	2.08	5.84	1.05	2.71	14.38	20.1	126.3	2.10
2-Methyl-heptanol-3	63.1	2.02	2.85	0.485	5.68	30.1	3.94	159	13.4
Octanol-1	71.2	2.02	2.93	.727	7.77	41.2	4.78	159	11.05

equation written in the form

$$V_{\mathrm{D}} = \tau RT/3\eta$$

for a spherical particle which may be compared with the volume V calculated from the density in the next column. As would be expected the Debye formula gives a molar volume much too small in every case. It has been suggested that a microscopic viscosity should be used in determining the frictional torque against which the molecule rotates rather than the macroscopic viscosity. To follow the Debye expression completely, the factor $(\epsilon_0 + 2)/(\epsilon_\infty + 2)$ should be included in the determination of the relaxation time. As this would decrease τ by a factor 0.3–0.8, the molar volumes so calculated would be even smaller.

The last column is illustrative of the reaction rate approach to the molecular mechanism for dipole rotation and for viscous flow. The expression

$$\frac{\eta V}{\tau RT} = e^{(\Delta F_\eta^{\ddagger} - \Delta F_\epsilon^{\ddagger})/RT}$$

is obtained by direct multiplication of the general expressions[22] for viscosity and the reciprocal of dipole relaxation time. This factor is apparently always greater than one and for most molecules about 2.5. This would correspond to about 0.5 kcal. difference in the free energies of activation for the two processes. The factor 2.5 is indicative of the fact that rotation alone is easier for the molecule than the combined motion of rotation and translation occurring in viscous flow. This is not unreasonable for in viscous flow the moving molecule must wait until some sort of hole is formed in front of it before it can proceed in the forward direction. Of course, there is the added possibility that the original equation for calculating the relaxation times from the dielectric measurements is in error. However, the more general equations[18] for the dispersion of the dielectric constant of polar liquids would give, as a rule, slightly smaller relaxation times, and, hence even larger differences in the free energies of activation. It is interesting to note that the factor is larger for the more symmetrical molecules, methylchloroform, *t*-butyl chloride, and *t*-amyl chloride, if the hydrogen bonded liquids, the alcohols, are not considered. This higher ratio indicates that, as would be expected, rotation alone as compared with rotation plus some translational motion is easier for the spherical molecules than for the linear molecules.

Although the molecule of methylchloroform is larger than that of chloroform, its symmetrical form, which permits it to rotate in the solid state,[23] gives it a lower relaxation time. The effect of molecular shape is even more evident in the case of *n*- and *t*-butyl chloride, the straight chain molecule having a relaxation time about 50% higher than that of the almost spherical molecule of the tertiary compound. Similarly, the differences in the pairs, *i*- and *t*-amyl chloride, and *n*- and *i*-amyl bromide, show how branching of the chain, which tends to change the molecular form from that of a rod toward that of a sphere, lowers the relaxation time. Conversely, lengthening of the molecule by adding to the length of the carbon chain increases the relaxation time, as does also increasing the polarizability of the molecule as evidenced by replacing methyl by chlorine, or chlorine by bromine or iodine, or bromine by iodine. In the case of a rod-shaped molecule, a single relaxation time is, obviously, an approximation, but, as the single value calculated tends to be lower, the greater the spread of the actual values, the effects just discussed should be more pronounced if the real values were known.

The high values of $\eta V/\tau RT$ for the two octyl alcohols are probably due to the fact that more than one relaxation time is involved, so that the single relaxation time obtained in the calculation is too low. From a comparison of the values of the dielectric constants for octanol-1 at low frequency, 9.94, and at 9.72 cm., 2.93, it is apparent that dispersion is largely complete. Now, for a single relaxation time, ϵ'' should be larger than $\epsilon - \epsilon_\infty$ for frequencies greater than the critical frequencies. However, the data of Table VI indicate that this is not the case for octanol-1. Only for very broad distributions of the relaxation times does $\epsilon - \epsilon_\infty$ become greater than ϵ'' for frequencies beyond half dispersion as can be seen from the curves reported by Yager[24] for a Gaussian distribution of relaxation times. Other distributions about a mean value give curves of similar characteristics. The low value of the static dielectric constant for 2-methyl-heptanol-3 may arise from a loose dimer or polymer formation different from that in octanol-1.

An empirical expression for the dielectric constant of liquids having a distribution of relaxation times has been proposed by Cole and Cole[19]

$$\epsilon^* - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty)/[1 + (i\omega\tau_0)^{1-\alpha}]$$

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[22] Ref. 20, p. 484, eq. (27), and p. 548, eq. (174).

[23] Turkevich and Smyth, This Journal, **62**, 2468 (1940).

[24] Yager, *Physics*, **7**, 434 (1936).

where ϵ^* is the complex dielectric constant and α is a distribution parameter, varying between zero and unity. In Table VII are recorded values of τ_0, a generalized relaxation time, and α for octanol-1 and 2-methylheptanol-3, which have been calculated from the data of Table VI. Included also are comparable compounds reported by Cole and Cole.[19]

TABLE VII

DISTRIBUTION OF RELAXATION TIMES IN HYDROGEN BONDED LIQUIDS

Substance	t, °C.	$\tau_0 \times 10^{11}$ sec.	α
Water[19]	19	0.94	0.09
Methyl alcohol[19]	19	6.4	0.13
Ethyl alcohol[19]	20	9.4	0.15
Propyl alcohol[19]	19	32	(0)
n-Butyl alcohol[19]	19	64	(0)
i-Amyl alcohol[19]	19	100	(0)
Octanol-1	25	133	0.494
2-Methylheptanol-3	25	5.75	0.111

With the exception of 2-methylheptanol-3, the relaxation times of the higher alcohols increase uniformly with increasing molecular length. The spread of distribution times, as indicated by α, is greater for octanol-1 than that for the other alcohols. However, the parentheses used by Cole and Cole indicate that, for propyl, butyl, and *i*-amyl alcohols, the results were somewhat doubtful. Again it is noted that the more spherical 2-methylheptanol-3 molecule rotates much more easily than the linear octanol-1, being comparable with the methyl alcohol molecule, which is, presumably, somewhat associated.

Summary

An apparatus has been constructed for the measurement of dielectric constant and absorption with electric waves which *in vacuo* have a length of 9.72 cm. Water has been measured at temperatures from 0 to 100°, and sixteen organic compounds have been measured at 25°. The viscosities of the organic compounds have also been measured.

The relaxation times of the molecules are calculated from the absorptions and used, in the case of water, to calculate the free energies, heats, and entropies of activation for the process of molecular rotation viewed in the light of the absolute reaction rate theory. The values of these thermodynamic quantities are comparable to those for viscous flow. The conclusion is drawn that the polarization of water is due to molecular orientation in the applied field rather than to proton transfer. The relaxation times of the organic molecules increase consistently with their size and the extent of their departure from spherical form. They are related to the behavior of the substances in viscous flow.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Preparation and Properties of Some New Trifluoromethyl Compounds

BY J. H. SIMONS AND EDWARD O. RAMLER[1]

In a previous paper[2] the methods of synthesis of trifluoromethyl compounds were discussed. At this time we can report on the preparation and properties of trifluoroacetyl chloride and trifluoroacetyl bromide. α-Trifluoroacetophenone was also prepared and its chemical and physical properties studied. This aromatic ketone is of interest as it is the first ketone of this type reported. Ketones in the aliphatic series containing the trifluoromethyl group have been prepared and studied.[3]

Preparations and Properties of Compounds

Trifluoroacetyl Chloride.—Barium trifluoroacetate was prepared according to the method of Swarts,[4] 36.3 g. (0.10 mole), dried in an oven at 110° for two hours, was placed in the reaction flask and 16 cc. (0.18 mole) of phosphorus trichloride added. An all glass system, consisting of a reaction flask and reflux condenser connected at the top to a dry ice-acetone trap, was used. The phosphorus trichloride was refluxed on a water-bath for eighteen hours. The product was distilled through a small low temperature column previously described by the authors.[5] There was obtained 14 g. (53%) of trifluoroacetyl chloride.

Anal. Calcd. for C_2F_3OCl: Cl, 26.79. Found: Cl, 27.21.

A small amount of this material was dissolved in about 15 cc. of dry ether, and the amide prepared by the addition

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[1] Present address: E. I. du Pont de Nemours and Co., Arlington, N. J.

[2] Simons, Bond and McArthur, THIS JOURNAL, **62**, 3477 (1940).

[3] Swarts, *Bull. classe sci., Acad. roy. Belg.*, **13**, 175 (1927); Fukuhara and Bigelow, THIS JOURNAL, **63**, 788 (1941).

[4] F. Swarts, *Bull. classe sci., Acad. roy. Belg.*, (5) **8**, 365 (1922).

[5] Ramler and Simons, *Ind. Eng. Chem., Anal. Ed.*, **14**, 430 (1942).