# *Dielectric Relaxation and Molecular Structure. I. Relaxation Time and Viscosity*

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Stokes' simple formula for a rigid sphere rotating in a viscous liquid was assumed by Debye[1] to be applicable to a sphere of molecular dimensions surrounded by other molecules of a similar size:

$$\tau=\frac{4\pi\eta a^3}{\boldsymbol{k}T} \tag{1}$$

in which $\eta$ is the ordinary viscosity[2] of the liquid, $a$ is the radius of the sphere, $\boldsymbol{k}$ is the Boltzmann constant, and $T$ is the absolute temperature.

Equation 1 has been employed widely for thirty years;[3] it has been applied even in the analysis of the relaxation times of nuclear magnetic resonance absorption.[4] It was soon discovered, however, that the molecular radius $a$ obtained from measurements of dielectric relaxation times, $\tau$, in either a liquid or a solution by the use of Eq. 1 is usually only a fraction of the actual radius.[3] In addition, the relaxation time does not follow the increase in viscosity for highly viscous liquids. The concept of internal or microscopic viscosity has been developed[5] to account for this anomaly; however, one can not place much reliance on the estimation of this viscosity of an unmeasurable nature.[6,7]

The object of the present paper is to postulate an empirical relation between the viscosity and the relaxation time and to compare it with Eq. 1. The ordinary viscosity alone will be considered here, since it seems desirable to deal only with measurable quantities. The dielectric measurements in the present report have been limited to dilute solutions, because the relaxation time measured in the liquid state is accompanied with ambiguity because of the choice of an arbitrary conversion ratio from the macroscopic relaxation time to the microscopic relaxation time.[3,8]

## Experimental

All the dielectric measurements reported below were made between $1\times10^7$ and $8\times10^7$ cycl./sec. (10 ~80 Mc./sec.) with a Hartshorn-Ward apparatus;[9] this measures the loss tangent ($\tan\delta=\varepsilon''/\varepsilon'$) in terms of the capacitance increment ($\Delta C$) corresponding to the half-width of the voltage-resonance curve of the cell-containing circuit.[10] The loss tangents were measured up to $2\times10^{-4}$. The whole apparatus was kept in an air-thermostat maintained at 25°C.

Our general procedure was checked by measuring a standard substance, benzophenone, in various solvents: *n*-hexane, benzene, carbon tetrachloride and Nujol.

In dilute solutions, both Debye and Onsager equations become:[8]

$$\tan\delta=\frac{(\varepsilon'+2)^2}{\varepsilon'}\,\frac{4\pi n\mu^2}{27\boldsymbol{k}T}\,\frac{\omega\tau}{1+\omega^2\tau^2} \tag{2}$$

where $\varepsilon'$ is the dielectric constant of the solvent, $n$ is the number of polar molecules per cubic centimeter, $\omega$ is the angular frequency, and $\tau$ is the relaxation time. When $\omega\tau\ll1$, this equation reduces to:

$$\tau=\frac{\tan\delta}{\omega c}\,\frac{6750\,\boldsymbol{k}T}{\pi\boldsymbol{N}\mu^2}\,\frac{\varepsilon'}{(\varepsilon'+2)^2} \tag{3}$$

where $\boldsymbol{N}$ is the Avogadro number and $c$ is the molar concentration. The constancy of $\tan\delta/\omega$ over a wide frequency range provides a simple test of Eq. 3. Table I contains results for benzophenone in two solvents, those with the lowest and the highest viscosities. The $\tan\delta/\omega$ values were found constant in all the solvents employed. Using a mean value, $\tan\delta/\omega=6.9\times10^{-12}$, and $\mu=2.94$ D, one finds $\tau=14.7\times10^{-12}$ sec. (14.7 p. sec.) at 25°C in hexane. This is in good agreement with Fairweather's value, 14.3 p. sec.[11] The results are further compared in Table II.

As shown by the above example, the value of the dipole moment in the particular medium is necessary for calculation. Consequently, measurements of dipole moments were carried out by

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[1] P. Debye, "Polar Molecules," Chemical Catalog, New York (1929).

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[3] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York (1955).

[4] N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

[5] E. Fischer, *Z. Elektrochem.*, **53**, 16 (1949).

[6] W. Kauzmann, *Rev. Mod. Phys.*, **14**, 12 (1942).

[7] K. Higasi, "Dielectric Relaxation and Molecular Structure," *Monogr. Res. Inst. Appl. Elec., Hokkaido University*, No. 9 (1961).

[8] Cf., for example, J. G. Powles, *J. Chem. Phys.*, **21**, 633 (1953); R. C. Miller and C. P. Smyth, *J. Am. Chem. Soc.*, **79**, 3310 (1957).

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[10] L. Hartshorn and W. H. Ward, *J. Inst. Elec. Engrs.*, **79**, 597 (1936); A. Aihara and M. Davies, *J. Colloid Sci.*, **11**, 671 (1956).

[11] A. Fairweather, *Proc. Phys. Soc.*, **B68**, 1038 (1955).

TABLE I. RELAXATION TIMES, $\tan\delta$ AND $\tan\delta/\omega c$ OF BENZOPHENONE

| | | | | |
|---|---|---|---|---|
| 1. Solvent, *n*-hexane: 0.2942 mol./l. | | | | |
| Freq. (Mc./sec.) | 16.65 | 33.43 | 55.3 | 75.0 |
| $\varepsilon'$ | 2.215 | 2.215 | 2.222 | 2.222 |
| $10^3\times\tan\delta$ | 0.22 | $0.42_8$ | $0.70_9$ | $0.96_3$ |
| $10^{12}\times\tan\delta/\omega c$ | $6.8_2$ | $6.9_6$ | $6.9_5$ | $6.9_3$ |
| $10^{12}\times\tau$(sec.) | $14._4$ | $14._7$ | $14._7$ | $14._7$ |
| 2. Solvent, Nujol: 0.2795 mol./l. | | | | |
| $\varepsilon'$ | $2.498_7$ | 2.500 | 2.506 | $2.499_3$ |
| $10^3\times\tan\delta$ | $3.37_8$ | $6.76_5$ | $10.96_1$ | $13.86_1$ |
| $10^{12}\times\tan\delta/\omega c$ | 115.5 | 115.2 | 112.9 | 105.2 |
| $10^{12}\times\tau$(sec.) | $238._9$ | $238._3$ | $233._2$ | $217._6$ |

TABLE II. RELAXATION TIMES OF BENZOPHENONE

| Solvent | Present wrok | | Literature | | Ref. |
|---|---|---|---|---|---|
| | $\eta$, c. p. s. | $\tau$, p. sec. | $\eta$, c. p. s. | $\tau$, p. sec. | |
| *n*-Hexane | 0.315/25°C | 14.7/25°C | 0.32/18°C | 14.3/18°C | 11 |
| Isooctane | 0.480/25°C | 18.4/25°C | — | — | |
| Benzene | 0.603/25°C | 20.4/25°C | | 20.4/23°C<br>22/19°C | 12*<br>13 |
| *p*-Xylene | — | — | | 20.0∼21.7/18°C | 14 |
| Carbon tetrachloride | 0.920/25°C | 25.0/25°C | 0.70/44°C | 26.5/44°C | 11 |
| Dioxane | 1.160/25°C | 24.0/25°C | — | — | |
| Nujol | 137.8/25°C | 238.0/25°C | 197/19°C | 295/19°C | 15 |

* Low frequency measurements based on Eq. 3.

the heterodyne-beat method and with the use of Halverstadt-Kumler's approximation.[16]

**Materials.**—All chemicals were of the best grade available and were purified before use; their m. p.'s or b. p.'s were checked against the values given in the literature.

## Results

Table III summarizes the results of the present measurements. Mixed solvents were employed for substances which were not soluble in pure solvents. Viscosity values are recorded of the solvent itself and also of the dilute solution with which the measurement was carried out; the symbols $\eta_{\mathrm{solv}}$ and $\eta_{\mathrm{solu}}$ are used to mark the distinction between them.

## Discussion

Plots of the observed relaxation times against the viscosities do not result in any satisfactory curve. On the other hand, when the logarithms of the relaxation times are plotted against the logarithms of the viscosities, an approximate linear relationship between $\log\tau$ and $\log\eta$ becomes noticeable, as may be seen in Figs. 1 and 2, in which plots are made in the logarithmic scale. For this reason, one can propose the following empirical equation:

$$\log\tau = A + x\log\eta \tag{4}$$

where $A$ and $x$ are constants relating to the substance alone under a given temperature. In Table IV the $A$ and $x$ values determined by the present series of experiments are recorded.

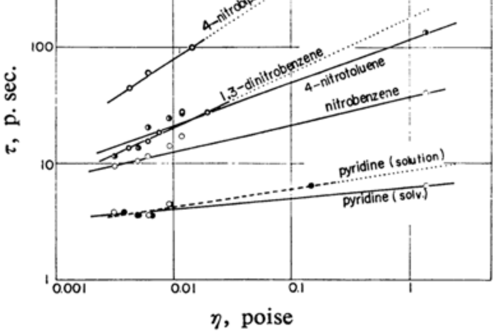

Fig. 1. Dependence of the logarithm of relaxation time of rigid molecules upon the logarithm of the viscosity. Full lines: $\eta_{\mathrm{solv}}$ employed; broken lines: $\eta_{\mathrm{solu}}$ employed.

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TABLE III. RELAXATION TIMES OBTAINED IN VARIOUS SOLVENTS (25°C)

1. Solute, Pyridine

| Solvent | $\mu$ D | $\eta_{solv}$ c. p. s. | $\eta_{solu}$ c. p. s. | $\tau$, p. sec. | | |
|---|---|---|---|---|---|---|
| | | | | 34.8 Mc. | 56.7 Mc. | 77.7 Mc. |
| *n*-Hexane | 2.25 | 0.315 | 0.379 | 3.75 | 3.78 | 3.92 |
| Isooctane | 2.27 | 0.480 | 0.498 | 3.67 | 3.54 | 3.64 |
| Benzene | 2.27 | 0.603 | 0.650 | 3.60 | 3.50 | 3.64 |
| Carbon tetrachloride | 2.35 | 0.920 | 0.942 | 4.51 | 4.42 | 4.60 |
| Nujol | 2.23 | 137.78 | 15.733 | 6.43 | 6.50 | 6.53 |

2. Solute, Diphenyl ether

| Solvent | $\mu$ D | $\eta_{solv}$ c. p. s. | $\eta_{solu}$ c. p. s. | $\tau$, p. sec. | | |
|---|---|---|---|---|---|---|
| | | | | 33.4 Mc. | 55.3 Mc. | 75.0 Mc. |
| *n*-Hexane | 1.09 | 0.315 | 0.728 | 4.95 | 5.17 | 5.38 |
| Isooctane | 1.11 | 0.480 | 0.818 | 5.48 | 5.56 | 5.47 |
| Benzene | 1.16 | 0.603 | 1.102 | 4.62 | 4.74 | 4.59 |
| Carbon tetrachloride | 1.13 | 0.920 | 1.418 | 7.67 | 7.69 | 8.11 |
| Nujol | 1.15 | 137.78 | 10.998 | 5.47 | 5.43 | 5.90 |

3. Solute, *m*-Dinitrobenzene

| Solvent | $\mu$ D | $\eta_{solv}$ c. p. s. | $\tau$, p. sec. | | | |
|---|---|---|---|---|---|---|
| | | | 16~17 Mc. | 33 Mc. | 55 Mc. | 75 Mc. |
| *n*-Hexane-Bz. | 3.92 | 0.415 | 13.1 | 13.1 | 13.7 | 14.3 |
| Isooctane-Bz. | 3.88 | 0.493 | 12.7 | 13.3 | 14.1 | 13.5 |
| Benzene | 3.84 | 0.603 | 14.7 | 15.7 | 15.6 | 15.8 |
| Carbon tetrachloride-Bz. | 3.84 | 0.746 | 18.3 | 18.6 | 18.1 | 18.9 |
| Dioxane | 4.00 | 1.160 | 27.4 | 27.3 | 27.3 | 28.3 |
| Nujol-Bz. | 3.73 | 1.921 | 27.2 | 27.6 | 26.6 | 27.8 |
| 4. Solute, Nitrobenzene | | | | | | |
| *n*-Hexane | — | 0.135 | 9.71 | 9.34 | 9.57 | 9.63 |
| Isooctane | — | 0.480 | 10.4 | 10.4 | 10.3 | 10.4 |
| Benzene | 4.03 | 0.603 | 11.3 | 11.0 | 11.1 | 12.0 |
| Carbon tetrachloride | — | 0.920 | 14.2 | 14.1 | 13.9 | 14.4 |
| Dioxane | — | 1.160 | 17.4 | 16.9 | 17.3 | 17.6 |
| Nujol | — | 137.78 | 40.8 | 41.2 | 39.2 | 40.1 |
| 5. Solute, *p*-Nitrotoluene | | | | | | |
| *n*-Hexane | 4.47 | 0.315 | 10.5 | 11.7 | 12.1 | 11.9 |
| Isooctane | 4.49 | 0.480 | 13.2 | 14.5 | 13.9 | 14.4 |
| Benzene | 4.43 | 0.603 | 21.6 | 20.2 | 20.1 | 20.6 |
| Carbon tetrachloride | 4.45 | 0.920 | 24.3 | 24.7 | 23.6 | 24.9 |
| Dioxane | 4.63 | 1.160 | 27.3 | 26.9 | 26.7 | 27.0 |
| Nujol | 4.54 | 137.78 | 139.9 | 131.2 | 127.7 | 134.5 |
| 6. Solute, *p*-Nitrobiphenyl | | | | | | |
| *n*-Hexane-Bz. | 4.55 | 0.420 | 44.7 | 43.4 | 43.3 | 44.8 |
| Benzene | 4.48 | 0.603 | 61.0 | 57.9 | 56.8 | 58.0 |
| Nujol-Bz. | 4.35 | 1.427 | 103.9 | 98.5 | 97.5 | 98.2 |
| 7. Solute, Benzophenone | | | | | | |
| *n*-Hexane | 2.94 | 0.315 | 14.4 | 14.7 | 14.7 | 14.7 |
| Isooctane | 3.04 | 0.480 | 18.3 | 18.4 | 20.1 | 18.9 |
| Benzene | 3.05 | 0.603 | 21.5 | 20.4 | 20.4 | 20.8 |
| Carbon tetrachloride | 3.06 | 0.920 | 26.2 | 24.6 | 25.5 | 25.4 |
| Dioxane | 3.24 | 1.160 | 24.5 | 23.6 | 24.4 | 24.7 |
| Nujol | 2.96 | 137.78 | 238.9 | 238.3 | 233.2 | 217.6 |
| 8. Solute, Benzil | | | | | | |
| *n*-Hexane-Bz. | 3.68 | 0.389 | 20.3 | 20.4 | 20.1 | 20.3 |
| Benzene | 3.71 | 0.603 | 24.0 | 24.8 | 25.2 | 25.7 |
| Carbon tetrachloride | 3.64 | 0.920 | 40.3 | 37.8 | 38.5 | 39.3 |
| Nujol-Bz. | 3.60 | 2.816 | 55.4 | 55.5 | 53.0 | 54.3 |

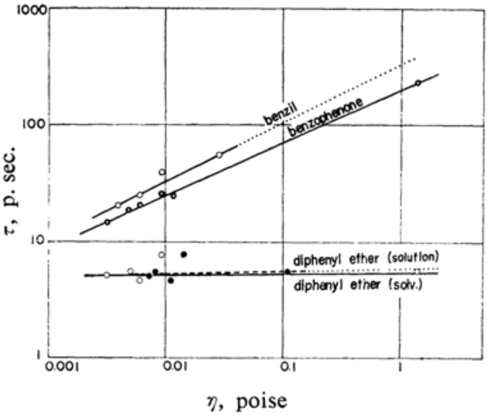

Fig. 2. Dependence of the logarithm of relaxation time of non-rigid molecules upon the logarithm of the viscosity.

TABLE IV. PARAMETER VALUES $A$ AND $x$ OBTAINED FROM THE PRESENT WORK

| Substance | $A$ | $x$ |
|---|---|---|
| Pyridine | $\overline{12}.796$ | 0.09 |
| | $\overline{12}.940$* | 0.16* |
| Nitrobenzene | $\overline{11}.575$ | 0.24 |
| 4-Nitrotoluene | $\overline{10}.071$ | 0.37 |
| 1, 3-Dinitrobenzene | $\overline{10}.246$ | 0.48 |
| 4-Nitrobiphenyl | $\overline{9}.204$ | 0.66 |
| Diphenyl ether | $\overline{12}.748$ | 0.01 |
| | $\overline{12}.778$* | 0.03* |
| Benzophenone | $\overline{10}.301$ | 0.46 |
| Benzil | $\overline{10}.532$ | 0.51 |

* $\eta_{\mathrm{solu}}$ is employed instead of $\eta_{\mathrm{solv}}$.

Alternatively, we may use $\eta_{\mathrm{solu}}$ instead of $\eta_{\mathrm{solv}}$ in examining the approximate linearity between $\log\tau$ and $\log\eta$. Pyridine in Fig. 1 and diphenyl ether in Fig. 2 show that Eq. 4 is equally valid for any case using either $\eta_{\mathrm{solv}}$ or $\eta_{\mathrm{solu}}$. The values of $A$ and $x$ marked by an asterisk in Table IV and the broken lines in Figs. 1 and 2 refer to the examination by the use of $\eta_{\mathrm{solu}}$.

The use of Eq. 2 requires that the dielectric absorption should be of the Debye type, which is not usually possible. In order to examine more fully the validity of Eq. 4, we have to refer to the results of the microwave measurements which account for the deviations from Debye's dispersion. In fact, this has been done by Higasi⁷⁾ and was repeated for the present work with equally satisfactory results. Table V records the values of $A$ and $x$ thus obtained.

Now we shall turn to the correlation between Stokes' formula and the new empirical equation. Equation 4 will become identical with Eq. 1 only when the following conditions are satisfied:

TABLE V. PARAMETER VALUES FROM THE LITERATURE

| Substance | $A$ | $x$ | $y$ | Ref. |
|---|---|---|---|---|
| 2, 2′-Dichloropropane | $\overline{12}.529$ | 0.07 | 0.23 | 17 |
| 2, 2′-Dinitropropane | $\overline{12}.851$ | 0.16 | 0.28 | 17 |
| *t*-Butyl chloride | $\overline{12}.423$ | 0.09 | 0.21 | 18 |
| Camphor | $\overline{11}.190$ | 0.16 | 0.29 | 19, 20 |
| 1, 3-Dichlorobenzene | $\overline{11}.373$ | 0.13 | — | 21 |
| Isoquinoline | $\overline{11}.591$ | 0.23 | 0.47 | 19, 22 |
| 1-Chloronaphthalene | $\overline{11}.712$ | 0.25 | 0.38 | 23 |
| 1-Bromonaphthalene | $\overline{11}.839$ | 0.27 | 0.41 | 23 |
| Acridine | $\overline{10}.845$ | 0.69 | 1.1 | 19 |
| 4-Bromobiphenyl | $\overline{9}.193$ | 0.66 | 0.92 | 19, 24 |

$$A=\log\frac{4\pi a^3}{kT}\;;\quad x=1 \qquad (5)$$

Tables IV and V both demonstrate that the $x$ parameter is not unity but, rather, is distributed within a wide range: $0<x<1$. This suggests that Stokes' formula is not applicable to a sphere of molecular dimensions.

It is interesting to examine the values of parameter $x$ in the light of molecular structure. For such rigid spherical molecules as 2, 2′-dichloropropane and *t*-butyl chloride, one will notice that the $x$ parameter is nearly zero; certainly, the Stokes spherical model is invalid. With an increase in distortion from sphericity, the parameter gradually increases: $x=0.24$ for nitrobenzene and $x=0.66$ for 4-nitrobiphenyl.

For molecules having freedom of internal rotation, the $x$ parameter becomes smaller. This tendency is demonstrated in Fig. 2 in the comparison of diphenyl ether with benzophenone; in the latter kind of molecules, the rotation of the benzene rings does not affect the dipole moment of the molecule, while in the former the molecular moment changes its direction by means of internal rotation.²⁵⁾ In connection with the internal motion of benzil,²⁶⁾ it is interesting to find that the $x$ parameter has the fairly large value of 0.46. This leads to a suggestion that benzil is practically a rigid molecule, which is in good agreement with the conclusions of the dipole work.²⁶⁾

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The trend of the $x$ parameter is a quantitative description of what has been said qualitatively by Smyth and his co-workers.(27) That is, if the shape of the molecule undergoing dipole rotation departs slightly from that of a sphere, the relaxation time has little dependence upon the viscosity since it can rotate without any considerable displacement of the surrounding molecules. Further, if the molecule is asymmetrical in shape, its rotation must involve the displacement of neighboring molecules and so the relaxation time should depend markedly upon the viscosity of the medium. The concept of the displacement of solvent molecules belongs to a mechanism entirely different from the Newtonian flow on which the Stokes model is theoretically based.

The relation between viscosity and temperature can be expressed by:

$$\eta = B \exp (E_\eta / RT) \qquad (6)$$

in which $E_\eta$ can be called the molar activation energy of viscosity. Similarly, we can write for the time of relaxation,

$$\tau = C \exp (E_\tau / RT) \qquad (7)$$

in which $C$ is considered to be independent of the temperature and $E_\tau$, the activation energy for relaxation.

If we take the ratio of $E_\tau$ to $E_\eta$ and denote it by $y$:

$$y = \frac{E_\tau}{E_\eta} \qquad (8)$$

then Eq. 6 will be transformed into:

$$\tau = C \exp (yE_\eta / RT) = (C/B^y) \cdot \eta^y$$

Or, we may write:

$$\log \tau = \log (C/B^y) + y \log \eta \qquad (9)$$

Eq. 9 will become identical to Eq. 4, if

$$x = y \quad \text{and} \quad A = \log (C/B^y) \qquad (10)$$

The values of $x$ obtained from various solvents using Eq. 4 are compared with the $y$ values obtained for Nujol by Kalman and Smyth(19) from Eq. 8. It is impressive to find in Table V that these two parameters are roughly parallel to each other; $x \simeq y$ and $0 < y \leqslant 1$. The $E_\tau / E_\eta$ ratio is not independent of solvents, and the second condition of Eq. 10 is satisfied only very approximately. These points seem to be reflected in the observed differences between $y$ and $x$ values.

Lastly, we may refer to the frequency dependence of the viscosity. One might point out that the viscosity of Nujol at the frequency of 10~80 Mc./sec. might be different from its static viscosity and that, consequently, the observed relationship might need to be reconsidered. However, this suggestion is untenable. If that be the case, one can not explain why the molecular shape can produce such a considerable variation in $x$ values.

## Conclusions

(1) Stokes' formula for a rotating sphere in a viscous medium cannot be applied to a sphere of molecular dimensions.

(2) There exists an empirical relation between the relaxation time, $\tau$, and the viscosity, $\eta$:

$$\log \tau = A + x \log \eta$$

in which the $x$ parameter has a value $0 < x \leqslant 1$.

(3) Through the $x$ parameter one can obtain some insight into the mechanism of rotation (internal rotation vs. overall rotation) or one can discuss the shape of the rotating unit.

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27) C. P. Smyth, Ref. 3, pp. 122–123.