BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 992—997 (1971)

Dielectric Relaxation and Molecular Structure. VI. Dielectric Measurements at the Frequency of 100 GHz

Kazuo Chitoku* and Keniti Higasi**
Research Institute of Applied Electricity, Hokkaido University, Sapporo
Masahiko Nakamura, Yoshinori Koga, and Hiroaki Takahashi
School of Science and Engineering, Waseda University, Shinjuku, Tokyo

(Received November 28, 1970)

This paper gives details of the equipment and the method of the measurement at 100 GHz. Dielectric constants and losses are measured at this frequency for ten organic molecules in benzene and four (aniline, phenol, and its derivatives) both in benzene and in dioxane. A majority of the molecules studied are of non-rigid configuration. Discussion is given of the relaxation times and the mechanism of internal rotation involved. Hydrogen bonding effects in aniline, phenol, and its derivatives are also discussed.

For many years a number of dielectric measurements have been carried out using a variety of frequency ranges. However, there are few dielectric data obtained in the range of very high frequency above 60 GHz, *i.e.*, below five millimeters in the wavelength. And this range of frequencies is a field which is still unexplored and need careful investigations.[1] For example, non-polar liquids such as benzene or carbon tetrachloride are found to show dielectric absorption in this frequency range[1] in a sharp contrast to the old belief that all the non-polar liquids should show no appreciable absorption in any range of frequencies.

According to Poley[2] polar liquids consisting of rigid molecules such as chlorobenzene and nitrobenzene are provided with an additional absorption at the high frequency end of millimeter band. This novel absorption became an object of intensive research.[3,4]

For a non-rigid molecule having a rotatable polar group or groups one finds two or more absorption peaks. The absorption due to internal rotation takes place in the millimeter range. For these reasons the dielectric measurements at a frequency of the wavelength less than 5 millimeters are of considerable interest.

In the present paper the writers wish to report on the millimeter wave apparatus for 100 GHz (3 mm), the method of measurements, the experimental results, and the dielectric relaxation times of the organic molecules obtained in dilute solution. Most of the substances chosen for the solute are of non-rigid configuration; and benzene was employed as solvent and for some solutes with hydrogen bonding capacity, *p*-dioxane was also used for comparison.

Apparatus

The experimental technique is based on the free space method.[5] For measuring dielectric constants and losses at 100 GHz the usual transmission line (wave guide) method is not much use since its upper limit is estimated to be about 75 GHz.[5] The apparatus is the microwave equivalent of Michelson interferometer and is of the same type with that of Garg, Kilp, and

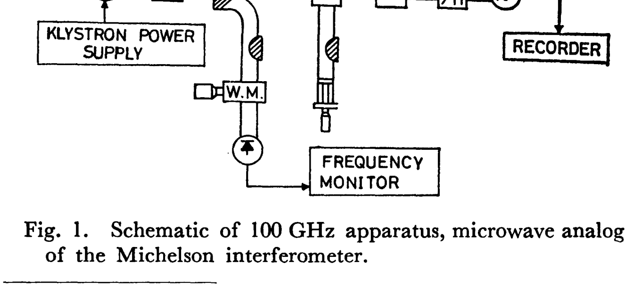

Fig. 1. Schematic of 100 GHz apparatus, microwave analog of the Michelson interferometer.

---

* Present address: Naka Works, Hitachi, Ltd., Katsuta, Ibaraki.

** Now at School of Science and Engineering, Waseda University, Shinjuku, Tokyo.

[1] N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, "Dielectric Properties and Molecular Behaviour," Van Nostrand Reinhold, London (1969), pp. 298—311.

[2] J. Ph. Poley, *J. Appl. Sci.*, **B4**, 337 (1955).

[3] G. W. Chantry and H. A. Gebbie, *Nature*, **208**, 378 (1965).

[4] M. Davies, G. W. F. Pardoe, J. Chamberlain, and H. A. Gebbie, *Trans. Faraday Soc.*, **66**, 273 (1970).

[5] N. E. Hill *et al.*, Ref. 1. See Chapter 2.

Smyth.[6,7] The schematic diagram of the apparatus is shown in Fig. 1.

The klystron (Oki 100 V 10 A) generates millimeter waves of about 3 mm in wavelength and its frequency is monitored by a cavity resonator (W 2203). The microwave energy is divided by a hybrid ring T (W 3701) in equal parts. Half passes through the transmitting horn N out into free space. A dielectric lens (TRGW 986) is used to produce a well-collimated beam, which traversed the liquid in the cell, reflected by the plunger, retraverses the liquid and finally is focussed by the lens back into the horn. In the reference arm the other half of the microwave energy from the hybrid is reflected by an adjustable plunger. The interference of the two beams takes place in the wave guide leading to the detective device and finally to the recorder (QPD 53).

Calculation of *n* and *k*

The complex index of refraction (n^*) of the material is defined as

$$n^* = n - jk \tag{1}$$

and the dielectric constant (ε') and the loss (ε'') of the same material are related to the above quantities according to

$$\left.\begin{aligned} \varepsilon' &= n^2 - k^2 \\ \varepsilon'' &= 2nk \end{aligned}\right. \tag{2}$$

The evaluation of n and k values are essentially the same as employed by Garg, Kilp, and Smyth.[6] The final equation for obtaining k is

$$\begin{aligned} \frac{I_{\max}(1) - I_{\min}(1)}{I_{\max}(2) - I_{\min}(2)} &= \exp\left(-2\beta_0 k[h_1 - h_2]\right) \\ &\times \left[\frac{(1+n) - (1-n)\exp(-4\beta_0 k h_1)}{(1+n) - (1-n)\exp(-4\beta_0 k h_2)}\right] \\ &\times \left[\frac{(1+n)^2 - (1-n)^2 \exp(-4\beta_0 k h_2)}{(1+n)^2 - (1-n)^2 \exp(-4\beta_0 k h_1)}\right]^2 \end{aligned} \tag{3}$$

The final electric intensity (I) at the detector has maxima and minima with the change of liquid thickness (h). The relative maximum ($I_{\max}$) and the adjacent relative minimum ($I_{\min}$) corresponding to a given liquid thickness h are observed; they are denoted by $I_{\max}(1)$, $I_{\min}(1)$ for h_1 and $I_{\max}(2)$ and $I_{\min}(2)$ for h_2, *etc.*. The phase constant β_0 is given by $\beta_0 = 2\pi/\lambda_0$ where λ_0 is the wavelength in air.

Smyth *et al.*[6] used an electronic computer to find n and k to fit the experimental curve. In the present work this formidable task of fitting was successfully replaced by a simple procedure which is based on a least-square method. (See Appendix.)

Purification of Materials

The organic compounds studied were all commercially available. Purchased materials of best grade were fractionally distilled before use. Solvents, benzene and *p*-dioxane, were carefully purified in the usual way.

Results

Measurements of ε' and ε'' for three to four dilute solutions for each solute were made and the so-called "slopes" a', a'', *etc.* were obtained on the assumption that the linear relationship of ε' and ε'' with the concentration (weight fraction) w_2 exists.

$$\left.\begin{aligned} \varepsilon' &= \varepsilon_1' + a'w_2 \\ \varepsilon'' &= \varepsilon_1'' + a''w_2\ ;\ \varepsilon_1'' \simeq 0 \\ \varepsilon_0 &= \varepsilon_{10} + a_0 w_2 \\ n_D{}^2 &= n_{1D}{}^2 + a_D w_2 \end{aligned}\right\} \tag{4}$$

in which subscript 1 refers to the pure solvent and 2 to the solute and the symbols have the usual meaning.

The relaxation time of a polar solute is obtained by the use of two equations.[8] We shall denote them by $\tau(1)$ and $\tau(2)$ in the following manner.

$$\left.\begin{aligned} \tau(1) &= \frac{1}{\omega} \cdot \frac{a''}{a' - a_\infty} \\ \tau(2) &= \frac{1}{\omega} \cdot \frac{a_0 - a'}{a''} \end{aligned}\right\} \tag{5}$$

There is no reliable method to evaluate a_∞. The most common approximation is to assume a_∞ to be equal to a_D. This may be equivalent to say that both atomic polarization term and correction due to Poley's absorption[2] can be neglected.

Grant[9] suggests the use of the following equation in evaluating ε_∞ (*viz.*, a_∞ in this case)

$$a_\infty(\equiv a_G) = a' - \frac{(a'')^2}{a_0 - a'} \tag{6}$$

We shall write the value given by Eq. (6) as a_G. The two values for relaxation times, $\tau(1)$ and $\tau(2)$, become identical with the use of this a_G value—the condition of $a_\infty = a_G$ may be a criterion for the pure Debye system with a single relaxation time. Contrary to this, $\tau(1)$ and $\tau(2)$ should have different vafues for a system with two Debye dispersions. They differ also for a system which obeys Cole-Cole's empirical rule.[8] Experimental values of a' and a'' obtained at about 100 GHz, *viz.*, 96.027 GHz are collected in Table 1. (See Eqs. (4) for the definition of a' and a''.) In the same table a_0 and a_D defined by Eqs. (4) are given together with a_G which is obtained from a', a'', and a_0 (see Eq. (6)).

Magee and Walker[10] proposed a new method for evaluating ε_∞ (hence a_∞) from the Cole-Cole arc for systems which really have two Debye dispersions. Their method was employed when sufficient data were available for the plot. When there are no reliable data, a tentative choice was made with the condition in mind that $a_D \leq a_\infty \leq a_G$.

In Table 2 a collection is given of experimental re-

---

[6] S. K. Garg, H. Kilp, and C. P. Smyth, *J. Chem. Phys.*, **43**, 2341 (1965).

[7] The writers are grateful to Professor C. P. Smyth, Princeton University, for providing them with an absorption material (Teflon impregnated with carbon) which was used in the cell cylinder.

[8] K. Higasi, Y. Koga, and M. Nakamura, This Bulletin, **44**, 988 (1971).

[9] One of the writers is grateful to Dr. E. H. Grant, London University, for discussions on the use of Eq. (6). See also N. E. Hill, *Trans. Faraday Soc.*, **59**, 344 (1963).

[10] M. D. Magee and S. Walker, *J. Chem. Phys.*, **50**, 2580 (1969).

Table 1. Slopes a', a'' obtained at 100 GHz in benzene (20°) and a_0, a_D, and a_G

Substance	a_0	a'	a''	a_D	a_G
Diphenyl ether	1.085	0.383	0.321	0.217	0.236
Dibenzyl ether	1.155	0.343	0.166	0.185	0.309
Benzophenone	5.982	0.608	0.550	0.282	0.551
Dibenzyl ketone	3.947	0.547	0.463	0.193	0.484
Chlorobenzene	2.477	0.263	0.497	0.052	0.151
Benzyl chloride	3.228	0.565	0.618	0.094	0.421
p-Xylene chloride	3.517	0.848	0.858	0.137	0.573
p-Dimethoxy benzene	2.551	0.564	0.481	0.060	0.447
p-Diethoxy benzene	2.130	0.474	0.399	0.018	0.378
Anisole	1.717	0.370	0.326	0.043	0.291
Aniline	2.806	1.141	0.678	0.219	0.865
(in dioxane)	4.407	1.239	0.521	0.514	1.153
Phenol	3.344	0.621	0.413	0.144	0.558
(in dioxane)	4.784	0.738	0.340	0.395	0.709
2,6-Dimethyl phenol	1.930	0.461	0.370	0.081	0.368
(in dioxane)	3.518	0.609	0.311	0.353	0.576
2,6-Di-*t*-butyl phenol	1.394	0.271	0.326	0.0	0.177
(in dioxane)	1.947	0.526	0.356	0.280	0.437

Table 2. Relaxation times $\tau(1)$ and $\tau(2)$ [This Experiment] and τ_0, τ_1, and τ_2 [Literature] in psec

Substance	$\tau(1)$	$\tau(2)$	Literature values
Diphenyl ether	3.2	3.6	τ_0 3.4[11] 4.0[12] 4.1[13]
Dibenzyl ether	1.7	8.1	τ_0 18[12]; τ_1 33[14] L; τ_2 3.9[14]L
Benzophenone	2.8	16.2	τ_0 16.4[15] 18.3[16] 20.4[17] 22[18]; τ_1 27[19] C; τ_2 3.5[19] C
Dibenzyl ketone	2.2	12.2	
Chlorobenzene	3.9	7.4	τ_0 8.3[6] 9.6[13] 8.6[17] 8.3[18] 10.8[20] L
Benzyl chloride	2.2	7.1	τ_0 9.9[15]; τ_1 14.0[22] 18.7[23] 20[21] 23.7[23]; τ_2 1.4[22] 2.3[23] 2.9[23] 4[21]
p-Xylene chloride	2.0	5.2	τ_0 3.0[24] 5.0[15]; τ_2 3.0[24]
p-Dimethoxy benzene	1.6	6.8	τ_0 6.2[25] 6.9[26] 9.7[27]; τ_1 8.5[22] 14.7[28] L; τ_2 0.75[22] 5.6[29]
p-Diethoxy benzene	1.4	6.9	
Anisole	1.6	6.9	τ_0 6.6[25] 7.6[15]; τ_1 9.0[22] 20[25]; τ_2 0.9[22] 3.2[29] 6.5[25]
Aniline	1.2	4.1	τ_0 9.78[30] L; τ_1 7.15[22] 22.2[28] L; τ_2 0.9[28] L 0.5[22]
Aniline (in dioxane)	1.2	10.1	τ_0 19.4[31]
Phenol	1.4	10.9	τ_0 9.3[32] C; τ_1 11.4[22]; τ_2 1.1[22]
Phenol (in dioxane)	1.6	19.7	
2,6-Dimethyl phenol	1.6	6.6	τ_0 5.3[33]; τ_1 13.7[33]; τ_2 3.4[33] 3.5[34]
2,6-Dimethyl phenol (in dioxane)	2.0	15.5	
2,6-Di-*t*-butylphenol	2.0	5.7	
2,6-Di-*t*-butylphenol (in dioxane)	2.4	6.6	

L liquid C cyclohexane T carbon tetrachloride

---

11) J. T. Vij and K. K. Srivastava, This Bulletin, **43**, 2313 (1970).

12) J. E. Anderson and C. P. Smyth, *J. Chem. Phys.*, **42**, 473 (1965).

13) J. Schneider, *ibid.*, **32**, 665 (1960).

14) K. Bergmann, D. M. Roberti, and C. P. Smyth, *J. Phys. Chem.*, **64**, 665 (1960).

15) E. Fischer, *Z. Naturforsch.*, **4a**, 707 (1949).

16) W. Jackson and J. G. Powles, *Trans. Faraday Soc.*, **42A**, 101 (1946).

17) K. Chitoku and K. Higasi, This Bulletin, **36**, 1064 (1963).

18) D. H. Whiffen and H. W. Thompson, *Trans. Faraday Soc.*, **42A**, 149 (1949); D. H. Whiffen, *ibid.*, **46**, 130 (1950).

19) D. Farmer and S. Walker, *Tetrahedron*, **22**, 111 (1966).

20) S. K. Garg and C. P. Smyth, *J. Chem. Phys.*, **42**, 1397 (1965).

21) E. M. Turner, W. W. Ehrhardt, G. Leone, and W. E. Vaughan, *J. Phys. Chem.*, **74**, 3543 (1970).

22) G. Klages and P. Knobloch, *Z. Naturforsch.*, **20a**, 580 (1965); P. Knobloch, *ibid.*, **20a**, 851 (1965).

23) W. P. Purcell, K. Fish, and C. P. Smyth, *J. Amer. Chem. Soc.*, **82**, 6299 (1960).

24) S. Dasgupta and C. P. Smyth, *ibid.*, **90**, 6318 (1968).

25) E. Forest and C. P. Smyth, *ibid.*, **86**, 3474 (1964).

26) E. Fischer, *Z. Naturforsch.*, **9a**, 909 (1954).

27) D. M. Roberti and C. P. Smyth, *J. Amer. Chem. Soc.*, **82**, 2106 (1960).

28) S. K. Garg and C. P. Smyth, *J. Chem. Phys.*, **46**, 373 (1967).

29) C. P. Smyth, "Molecular Relaxation Processes," Chem. Soc. Special Publ. No. 20, Chemical Society, London (1966), p. 6.

30) E. Fischer, *Z. Physik*, **127**, 49 (1949).

31) K. Chitoku and K. Higasi, This Bulletin, **39**, 2160 (1966).

32) E. Fischer and R. Fessler, *Z. Naturforsch.*, **8a**, 177 (1953).

33) F. K. Fong and C. P. Smyth, *J. Amer. Chem. Soc.*, **85**, 1565 (1963).

34) A. Aihara and M. Davies, *J. Colloid Sci.*, **11**, 671 (1965).

laxation times in the units of psec (10^{-12} sec). Solvent is benzene if not stated; and temperature is 20°C for the present work and 15°—25° for the literature values. $\tau(1)$ and $\tau(2)$ are calculated by the use of a', a'', a_0, and a_D values recorded in Table 1. Since a_D is used instead of a_∞ throughout, $\tau(1)$ calculated from Eq. (5) is too low in general. Regarding the literature values τ_0 denotes the average relaxation time, τ_1 the relaxation time for overall rotation and τ_2 the relaxation time for internal rotation.

Discussion

Table 2 shows that diphenyl ether has two close values for the relaxation time $\tau(1)=3.2$ psec and $\tau(2)=3.6$ psec and according to Table 1 a_G is found to be near a_D. In contrast to this benzophenone has $\tau(1)=2.8$ psec and $\tau(2)=16.2$ psec and a_G is much larger than a_D. If an intermediate value 0.51 between a_D and a_G is taken for a_∞, $\tau(1)$ will become larger, *viz.*, 9.5 psec. Assuming that diphenyl ether and benzophenone have the same relaxation mechanism associated with $\tau_1=19.9$ psec and $\tau_2=3.31$ psec one will find the weight factor for internal rotation to be very big, *viz.*, $C_2=0.92$, in diphenyl ether, while the same factor is very small in benzophenone, *viz.*, $C_2=0.06$ for $\tau(1)=9.5$ psec and $\tau(2)=16.2$ psec.—The method of the analysis is given in the preceding paper.[8] These findings are in good agreement with the experimental results in the liquid state[35] and with the internal rotation mechanism based on the mesomeric effects.[36]

Two opposite views are available in connection with the dielectric anomaly of diphenyl ether.[37] One is based on the belief that the molecular moment of diphenyl ether lies in the direction of the line dividing the C–O–C angle of the molecule in two equal parts. This makes overall rotation, rotation of the whole molecules, to be the only cause of dielectric absorption. This is because rotation of two rings will not produce any change in the direction of the molecular moment. The other view[36] is based on the assumption that there might be a dipole component perpendicular to the line dividing the C–O–C angle equally and if so, this component (due to mesomerism) would be appreciable in diphenyl ether and very small in benzophenone. The advantage of the second view is that rotation of two rings alone can produce a change in the orientation of the molecular moment.

According to the former view one has to assume a special kind of overall rotation coupled with rotation of two rings[38] which would not occur so frequently. The weakness of the second mechanism is the lack of direct evidence for it[39]—although there is no reliable evidence against it[12,40,41] either.

Introduction of two CH_2 groups between O or C=O and two aromatic rings in the molecule of diphenyl ether or benzophenone will reduce the mesomeric effect and at the same time it will give a greater flexibility to the molecule.[42] It is interesting to find in this connection that $\tau(2)$ in Table 2 increases with the order: diphenyl ether, dibenzyl ether, dibenzyl ketone, and benzophenone.

Relaxation times for chlorobenzene (Table 2) are $\tau(1)=3.9$ psec and $\tau(2)=7.4$ psec, these being obtained on the assumption $a_\infty=a_D=0.05$. Contrary to this, or better a_∞ is estimated from the Cole-Cole plot, —we shall call it a_{CC}; Garg, Kilp, and Smyth[6] provided $a_{CC}=0.15$ which happens to be equal to a_G (Table 1). If this a_{CC} is used as a_∞, $\tau(1)=\tau(2)=7.4$ psec and Poley's absorption[2] will not exist or will be too weak to be detected at 100 GHz.

If a little smaller value $a_\infty=0.11$ is tentatively chosen, one would reach a conclusion that such an absorption does exist at the shorter end of millimeter band. For example, a weak absorption with $\tau_2=0.5$ psec, $C_2=0.1$ with the molecular rotation $\tau_1=8.5$ psec will be expected[8] on the assumption of two Debye processes. One of us (Takahashi)[43] confirmed Poley's absorption at about 2000 GHz (60 cm^{-1}) by a far infra-red spectrometer (FIS-3).

Dielectric relaxation of benzyl chloride has been analysed by Knobloch[22] and Purcell *et al.*[23]; the former gives $\tau_1=14.0$ psec, $\tau_2=1.4$ psec, $C_2=0.30$ while the latter gives two sets of $\tau_1=18.7$, $\tau_2=2.9$, and $\tau_1=23.7$, $\tau_2=2.3$ (all in psec). The present data lead to $\tau_1=12.4$ psec, $\tau_2=2.48$ psec and $C_2=0.24$[8] with the use of $a_{CC}=0.31$.[23] It appears fairly certain that there exist two dispersion regions in this molecule.

It is not clear, however, whether *p*-xylene chloride has such two relaxation processes or not. If $a_\infty=a_G=0.573$ is true, $\tau(2)=5.2$ psec will be the intramolecular relaxation time. On the other hand if the group rotation has a shorter relaxation time 1—2 psec,[22] we shall have to assume some contribution from overall rotation. An analysis[8] of the present data gives $\tau_1=11.6$ psec, $\tau_2=1.65$ psec, $C_2=0.25$ with $a_\infty=0.25$; or $\tau_1=11.6$ psec, $\tau_2=3.31$ psec, $C_2=0.55$ with $a_\infty=0.48$.

It is possible that both *p*-dimethoxy benzene and *p*-diethoxy benzene have two distinct relaxation processes, *viz.*, due to overall rotation as well as to internal rotation.[44] This is because if two methoxy or two ethoxy groups have freedom of rotation around the C–O axes, the components of the two mesomeric moments along the direction of the molecular axis would not cancel each other.

Now, consider the mesomeric moment arising from the upper OCH_3 group (see Fig. 2). The mesomeric moment depends upon the angle of rotation, φ_1, measured from the plane of the benzene ring.[45]

---

[35] W. E. Vaughan and C. P. Smyth, *J. Phys. Chem.*, **45**, 98 (1961); W. E. Vaughan, W. S. Lovell, and C. P. Smyth, *J. Chem. Phys.*, **36**, 535 (1962).

[36] K. Higasi, This Bulletin, **35**, 632 (1962); K. Higasi and C. P. Smyth, *J. Amer. Chem. Soc.*, **82**, 4759 (1960).

[37] K. Higasi, "Dipole, Molecule and Chemistry," Hokkaido Univ., Sapporo (1965). Chapter II, pp. 19—36.

[38] F. K. Fong, *J. Chem. Phys.*, **40**, 132 (1964).

[39] K. Chitoku and K. Higasi, *Bull. Res. Inst. Appl. Elec.* (Hokkaido Univ.), **19**, 32 (1967).

[40] K. Higasi, *Kagaku to Kogyo*, **15**, 118 (1962).

[41] D. B. Farmer and S. Walker, *Trans. Faraday Soc.*, **63**, 966 (1967).

[42] A. Aihara, Private Communication.

[43] H. Takahashi, to be published.

[44] K. Higasi, "Dielectric Relaxation and Molecular Structure," Hokkaido Univ., Sapporo (1961), p. 34.

[45] K. Higasi, H. Baba, and A. Rembaum, "Quantum Organic Chemistry," Interscience, New York (1965), p. 157.

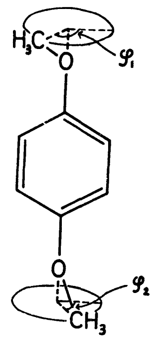

Fig. 2. Internal rotation in *p*-dimethoxybenzene and two angles of rotation, φ_1 and φ_2.

$$\mu_{\rm m}(\text{upper}) = \mu_{\max} \cos^2 \varphi_1$$

Similarly for the lower OCH$_3$ group

$$\mu_{\rm m}(\text{lower}) = \mu_{\max} \cos^2 \varphi_2$$

where φ_2 is the angle of rotation of the lower group. The component along the molecular axis is

$$\mu_{\rm m}(\text{upper}) - \mu_{\rm m}(\text{lower}) = \mu_{\max}(\cos^2 \varphi_1 - \cos^2 \varphi_2)$$

The average $<\cos^2 \varphi_1 — \cos^2 \varphi_2>$ is 1/4 for free rotation and is not equal to zero in general. Contributions from overall rotation would be appreciable unless the maximum mesomeric moment $\mu_{\max}$ of a methoxy group attached to a benzene ring is very small.[44]

The present data of $\tau(1)$ and $\tau(2)$ seem to support the above view, since the weight factor for molecular rotation $1-C_2$ is found to be quite large in several analyses[8] of the data. For example, for *p*-dimethoxy benzene $\tau_1=11.55$ psec, $\tau_2=1.65$ psec, $C_2=0.20$ with $a_\infty=0.30$ and for *p*-diethoxybenzene $\tau_1=11.55$ psec, $\tau_2=1.65$ psec, $C_2=0.20$ with $a_\infty=0.25$. These data can well be compared with the result of Klages and Knobloch's[22] analysis on *p*-dimethoxybenzene, or with Klages and Zenteks[46] $C_2=0.17$, $\tau_1=8.8$ psec, $\tau_2=(0.4)$ psec. More recently Vaughan *et al.*[47] give $C_2=0.13$ with $\tau_1=6.2$ psec and $\tau_2=0.9$ psec for liquid. However, there is uncertainty regarding the choice of a_∞. Anisole is in accord with $\tau_1=9.90$ psec, $\tau_2=1.65$ psec, $C_2=0.16$ with $a_\infty=0.21$. Again, it would be most desirable to have a reliable a_∞ value in order to find how important is the contribution of overall rotation.

Last group of four molecules are studied by the use of two solvents, benzene and dioxane, with a view to examining the hydrogen bonding effects of the solute with the solvent. According to the previous method of analysis[8] of two mean relaxation times $\tau(1)$ and $\tau(2)$ obtained at this high frequency one can make a very crude estimate of τ_1 and τ_2. The relaxation time τ_1 for overall rotation is closer $\tau(2)$ than to $\tau(1)$ and the relaxation time for internal rotation τ_2 is near to the observed $\tau(1)$ value. Recorded $\tau(1)$ values of these molecules are about 1—3 psec which is in good agreement with τ_2 for the OH and also for the NH$_2$ groups given by Knobloch.[48] In contrast to $\tau(1)$, $\tau(2)$ varies greatly with solutes and solvents and has values 4—20 psec. The ratio of $\tau(2)$ obtained in dioxane to that in benzene, $\tau_{\rm D}/\tau_{\rm B}$, is 2.48 (aniline), 1.81 (phenol), 2.36 (2,6-dimethyl phenol) and 1.16 (2,6-di-*t*-butyl phenol). The ratio of viscosities of two solvents is 1.2836 : 0.6466=1.99 : 1, while $\tau_{\rm D}/\tau_{\rm B}$ for chlorobenzene and nitrobenzene are 1.57 and 1.51 respectively. The observed high increase of τ values from benzene to dioxane in aniline, phenol, and 2,6-dimethyl phenol is an indication that an oxygen atom of dioxane forms a hydrogen bond with amino-hydrogen atoms in aniline or with the hydrogen atom in phenol or of its derivative.[31] However, on account of the steric hindrance of the bulky substituents the OH group in 2,6-di-*t*-butyl phenol is not able to form a hydrogen bond with the solvent molecule. It is impressive to find small $\tau(2)$ values for this molecule both in benzene and dioxane. The group rotation seems to predominate in this molecule, as is the case of 2,4,6-tri-*t*-butyl phenol in decalin.[49] Further, the solute molecules tend to associate through hydrogen bonds. This association seems to take place in case of phenol in benzene.[50] Without such an effect the ratio $\tau_{\rm D}/\tau_{\rm B}$ of phenol would possibly be much larger than the observed.

Appendix

1. *Calculation of n.* The real part of the refractive index n is expressed as

$$n = \sqrt{\frac{\left(\dfrac{\lambda_0}{\lambda_d}\right)^2+\left(\dfrac{\lambda_0}{\lambda_c}\right)^2}{1+\left(\dfrac{\lambda_0}{\lambda_c}\right)^2}} \tag{A-1}$$

where λ_0, λ_d, and λ_c are the wavelength in air, the wavelength in the sample and the cut-off wavelength, respectively.

2. *Calculation of k.* The imaginary part of the refractive index k is calculated according to Eq. (3) by a least square method. Eq. (3) can be replaced in the following integrated form (A-2) using the relation:

$$h_m = \frac{1}{2} m\lambda_d$$

and

$$\beta_0 = 2\pi/\lambda_0$$

where $m=1, 2, \cdots, t$.

$$Y_m = -A_m k - B_m(k) + C \tag{A-2}$$

where

$$Y_m = \ln[I_{\max}(m) - I_{\min}(m)]$$

$$A_{\rm m} = \frac{2\pi\lambda_d}{\lambda_0} m$$

$$B_m(k) = \ln\frac{\left[(1+n)^2-(1-n)^2\exp\left(-\dfrac{4\pi\lambda_d k m}{\lambda_0}\right)\right]^2}{\left[(1+n)-(1-n)\exp\left(-\dfrac{4\pi\lambda_d k m}{\lambda_0}\right)\right]}$$

C is an integration constant.

---

46) G. Klages and A. Zentek, *Z. Naturforsch.*, **16a**, 1016 (1961).

47) W. E. Vaughan, S. B. W. Roeder, and T. Provder, *J. Chem. Phys.*, **39**, 701 (1963).

48) P. Knobloch, *Ber. Bunsenges. Phys. Chem.*, **69**, 296 (1965).

49) M. Davies and R. J. Meakins, *J. Chem. Phys.*, **26**, 1584 (1957).

50) K. Higasi, This Bulletin, **25**, 159 (1952).

The observed values of Y_m are expressed in a matrix form.

$$\tilde{\mathbf{Y}}^{\circ} = (Y_1{}^{\circ}, Y_2{}^{\circ}, \cdots, Y_t{}^{\circ})$$

The unknown parameters in Eq. (A-2) are k and C. Therefore it is desired to obtain the values of k and C which give the calculated values of $\tilde{\mathbf{Y}}=(Y_1, Y_2, \cdots, Y_t)$ closest to $\tilde{\mathbf{Y}}^{\circ}$.

This may be done by the following procedure. Let k^{I} and C^{I} be the first guessed values of k and C and $\tilde{\mathbf{Y}}^{\mathrm{I}}=(Y_1{}^{\mathrm{I}}, Y_2{}^{\mathrm{I}}, \cdots, Y_t{}^{\mathrm{I}})$ be the calculated values of $\tilde{\mathbf{Y}}$ using k^{I} and C^{I}. To get the corrections $\varDelta k^{\mathrm{I}}$ and $\varDelta C^{\mathrm{I}}$ from the difference $\varDelta\mathbf{Y}=\mathbf{Y}^{\circ}-\mathbf{Y}^{\mathrm{I}}$, let us assume the corrected values to be k^{II} and C^{II} and the calculated values to be $\tilde{\mathbf{Y}}^{\mathrm{II}}=(Y_1{}^{\mathrm{II}}, Y_2{}^{\mathrm{II}}, \cdots, Y_t{}^{\mathrm{II}})$. The purpose of the least square method is to minimize the value of S which is expressed as:

$$S = (\tilde{\mathbf{Y}}^{\circ}-\tilde{\mathbf{Y}}^{\mathrm{II}})\mathbf{W}(\mathbf{Y}^{\circ}-\mathbf{Y}^{\mathrm{II}})$$

where $\mathbf{W}$ is a diagonal matrix whose element w_l is the weight factor of $Y_l{}^{\circ}$.

An assumption is made that the variation of $\mathbf{Y}$ is linearly proportional to $\varDelta k$ and $\varDelta C$ when they are very small. That is:

$$\mathbf{Y}^{\mathrm{II}} - \mathbf{Y}^{\mathrm{I}} = \mathbf{J}^{\mathrm{I}}\varDelta\mathbf{K}^{\mathrm{I}}$$

where $\mathbf{J}^{\mathrm{I}}$ is a Jacobian matrix expressed as:

$$\mathbf{J}^{\mathrm{I}} = \begin{pmatrix} \dfrac{\partial Y_1{}^{\mathrm{I}}}{\partial k^{\mathrm{I}}} & \dfrac{\partial Y_1{}^{\mathrm{I}}}{\partial C^{\mathrm{I}}} \\ \dfrac{\partial Y_2{}^{\mathrm{I}}}{\partial k^{\mathrm{I}}} & \dfrac{\partial Y_2{}^{\mathrm{I}}}{\partial C^{\mathrm{I}}} \\ \vdots & \vdots \\ \dfrac{\partial Y_t{}^{\mathrm{I}}}{\partial k^{\mathrm{I}}} & \dfrac{\partial Y_t{}^{\mathrm{I}}}{\partial C^{\mathrm{I}}} \end{pmatrix}$$

and

$$\varDelta\mathbf{K}^{\mathrm{I}} = \begin{pmatrix} \varDelta k^{\mathrm{I}} \\ \varDelta C^{\mathrm{I}} \end{pmatrix}$$

then

$$S = (\varDelta\tilde{\mathbf{Y}}^{\mathrm{I}} - \varDelta\tilde{\mathbf{K}}^{\mathrm{I}}\tilde{\mathbf{J}}^{\mathrm{I}})\mathbf{W}(\varDelta\mathbf{Y}^{\mathrm{I}} - \mathbf{J}^{\mathrm{I}}\varDelta\mathbf{K}^{\mathrm{I}}) \qquad \text{(A-3)}$$

In order to mimimize S, the differenciation of S by $\varDelta\mathbf{K}^{\mathrm{I}}$ must be zero. One obtains the following simultaneous linear equation

$$\tilde{\mathbf{J}}^{\mathrm{I}}\mathbf{W}\mathbf{J}^{\mathrm{I}}\varDelta\mathbf{K}^{\mathrm{I}} = \tilde{\mathbf{J}}^{\mathrm{I}}\mathbf{W}\varDelta\mathbf{Y}^{\mathrm{I}} \qquad \text{(A-4)}$$

This equation may be solved if $|\tilde{\mathbf{J}}^{\mathrm{I}}\,\mathbf{W}\,\mathbf{J}^{\mathrm{I}}| \neq 0$ which is usually satisfied. Using the above calculated values of $\varDelta\tilde{\mathbf{K}}^{\mathrm{I}}=(\varDelta k^{\mathrm{I}}. \varDelta C^{\mathrm{I}})$ the most appropriate second guessed values k^{II} and C^{II} are obtained.

$$k^{\mathrm{II}} = k^{\mathrm{I}} + \varDelta k^{\mathrm{I}}$$

$$C^{\mathrm{II}} = C^{\mathrm{I}} + \varDelta C^{\mathrm{I}}$$

The final values of k and C which give the best fit between observed and calculated values of $\mathbf{Y}$ can be obtained by repeating this process until S cannot be reduced any further.

We are grateful to Professor S. Nagakura, the University of Tokyo, and Prof. H. Baba, Hokkaido University, for their invaluable help in the present work. Thanks are due to the Ministry of Education and the Toray Science Foundation for the financial aid.