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Dielectric Relaxation and Molecular Structure. III. Relaxation Times of Aniline Derivatives in Benzene and Dioxane

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A brief description is made of the experimental methods for measuring microwave dielectric constants and losses of solutions in the frequency range 10—50 Gc./sec. Dielectric data obtained in this experiment were analysed from the viewpoint of molecular interaction between the solute and the solvent molecules. Six benzene derivatives with the amino group, aniline (A), *N*, *N'*-dimethylaniline (B), *N*, *N'*-diethylaniline (C), 2, 6-dimethylaniline (D), *p*-nitroaniline (E) and *N*-methylaniline (F) were chosen as solutes. Benzene and dioxane were used as solvents. The relaxation times of A, D and E obtained in dioxane are about three or five times larger than the corresponding relaxation times in benzene. The relaxation times of B and C in dioxane were about twice or one and half of the corresponding values obtained in benzene. The dielectric behavior of F is intermediate between A and B. These results are attributable to the hydrogen-bond formation between an oxygen atom of the dioxane molecule and an amino-hydrogen atom (F) or atoms (A, D and E).

According to Eyring[1,2] the process of molecular rotation requires an activation energy sufficient to overcome the energy barrier separating the two mean equilibrium positions with opposite directions of the dipole; and hence, the relaxation time τ is given by the rate expression

1) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York (1941), Chapter 9.

2) W. Kauzmann, *Rev. Mod. Phys.*, **14**, 12 (1942).

Table I. Relaxation times τ (p. sec.) measured in cyclohexane and carbon tetrachloride and differences in free energies $\Delta F_2^* - \Delta F_1^*$ (cal./mole)

Substance	t, °C	CCl_4	C_6H_{12}	τ_2/τ_1	$\Delta F_2^* - \Delta F_1^*$
Chlorobenzene	25	12.8[a]	7.6[a]	1.68	310
Nitrobenzene	25	19.6[a]	11.8[a]	1.66	300
t-Butyl chloride	20	3.4[b]	1.6[c]	2.12	440
Chloroform	20	5.0[d]	3.2[d]	1.56	260
Camphor	20	10.7[d]	7.1[d]	1.51	240
Cyclohexyl chloride	25	14.3[a]	9.2[a]	1.55	260
Cyclohexanone	25	8.7[e]	4.4[e]	1.98	400
Pyridine	25	7.8[a]	5.3[a]	1.47	230

a) H. Hase, *Z. Naturforsch.*, **8a**, 695 (1953).
b) A. T. Curtis, P. L. McGeer, G. B. Rathmann and C. P. Smyth, *J. Am. Chem. Soc.*, **74**, 644 (1952).
c) A. D. Franklin et al., Ref. 12.
d) D. H. Whiffen, *Trans. Faraday Soc.*, **46**, 130 (1950).
e) F. Dieringer, *Z. Physik*, **145**, 184 (1956).

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta F^*}{RT}\right) = \frac{h}{kT} \exp\left(\frac{-\Delta S^*}{R}\right) \exp\left(\frac{\Delta H^*}{RT}\right) \quad (1)$$

where h is the Planck constant, k is the Boltzmann constant, T is the absolute temperature, R is the gas constant; ΔF^*, ΔH^* and ΔS^* are the free energy, the enthalpy, and the entropy, of activation for dipole relaxation.

If two relaxation times τ_1 and τ_2 of the same substance are obtained at the same temperature in two different solvents 1 and 2, the ratio τ_2/τ_1 will be given by Eq. 2.

$$\frac{\tau_2}{\tau_1} = \exp\left(\frac{\Delta F_2^* - \Delta F_1^*}{RT}\right) = \exp\left(\frac{\Delta S_1^* - \Delta S_2^*}{RT}\right) \exp\left(\frac{\Delta H_2^* - \Delta H_1^*}{RT}\right) \quad (2)$$

in which ΔF_1^* and ΔF_2^* are the free energies of activation in the two solvents 1 and 2; and similarly, ΔS_1^*, ΔS_2^*, ΔH_1^* and ΔH_2^* represent the entropies and the enthalpies in the corresponding solvents.

In contrast to this, the familar Debye-Stokes equation[3] is expressed by

$$\tau = \frac{4\pi\eta a^3}{kT} \quad (3)$$

in which η is the viscosity of the liquid and a is the radius of the polar spherical molecule. This equation fails to explain why the relaxation time of a given polar molecule obtained in carbon tetrachloride differs from that obtained in cyclohexane in spite of the fact that these solvents have almost the same viscosity (Table I).

On the basis of Eq. 2, however, we can explain the observed difference between two relaxation times as indicating that ΔF_2^* in carbon tetrachloride is much larger than ΔF_1^* in cyclohexane. If ΔS_1^* is not much different from ΔS_2^*, the energy term ΔH^* in the activation process will become larger in carbon tetrachloride. One may say from this that carbon tetrachloride hinders much more effectively the rotation of the solute dipole than cyclohexane does. Perhaps the forces acting between the solute and carbon tetrachloride molecules are fairly large;* indeed, some molecular compounds with appreciable heats of formation have been detected in systems with carbon tetrachloride.[4] It is to be noted in this connection that the difference of ΔF^* by a few hundreds calories per mole results in a considerable difference in dielectric relaxation times.

For this reason dielectric relaxation times might be considered useful clue for studying interactions between the solute and solvent molecules. The present paper deals with an examination on this possibility.

Experimental Apparatus

Dielectric constants and losses are measured at four frequencies, 1 Mc./sec., 9.33 Gc./sec., 24.15 Gc./sec. and 48.00 Gc./sec. The detailed description of the apparatus and the experimental procedure is given in the following. The measurements at 1 Mc./sec. are based on the usual heterodyne beat method.

Measurements at Frequencies 9.33 and 24.15 Gc./sec.—Figure 1 shows the block diagram of 24.15 Gc. apparatus which is based on the standing wave method as developed by Heston, Franklin,

3) P. Debye, "Polar Molecules," Chemical Catalogue, New York (1929), Chapter 5.

* Or, one may consider cyclohexane an anomalous solvent instead (F. Hufnagel and H. Klip, *Z. Naturforsch.*, **18a**, 769 (1963).

4) A. Kuboyama, *Symposium on Electronic States*, **9**, 13 (1954); W. F. Wyatt, *Trans. Faraday Soc.*, **24**, 429 (1928), **25**, 43, 49 (1929); P. Traynard, *Bull. Soc. Chim.*, **12**, 98 (1945).

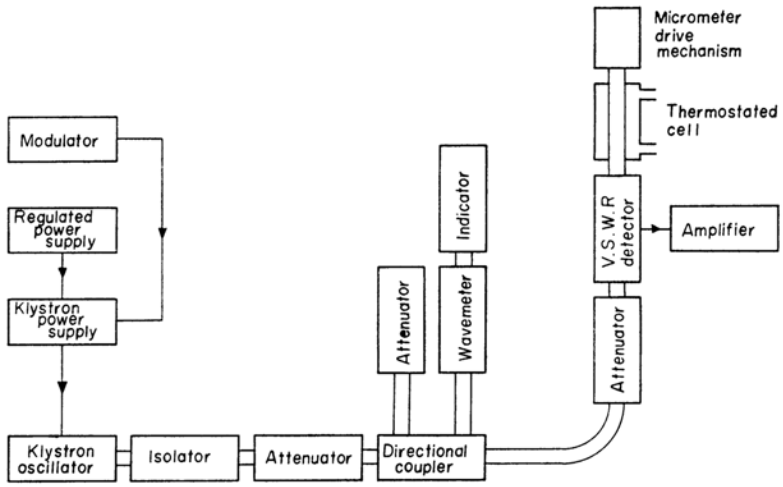


Fig. 1. Block diagram of 24 Gc. apparatus.

Hennelly and Smyth.[5] It consists of a klystron as the energy source, wave guides for transmitting the energy, and a traveling probe for detecting the energy (Fig. 1). A mica window is used in a wave guide to separate the wave guide into two parts, the top part of which forms the dielectric cell into which is put the solution being measured. A micrometer driven plunger is mounted in this cell (Fig. 2). The energy wave entres the wave guide, passes through the liquid, and then comes in contact with open circuited plunger, which reflects the wave back into the wave guide and produces a standing wave.

The experimental process is as follows. With the liquid in the cell and the plunger at the cell window, the traveling probe is set to a minimum

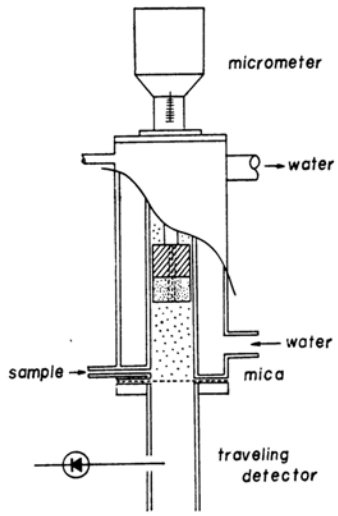


Fig. 2. Dielectric cell for use at 24 Gc.

power position. Then the plunger is turned upward, increasing the depth of the liquid, until another power minimum is noticed, i. e., a second node. The distance between two minima is equal to $\lambda_d/2$. For low loss materials the dielectric constant ε' is given by

$$\varepsilon' = \left(\frac{\lambda_0}{\lambda_d}\right)^2 + \left(\frac{\lambda_0}{\lambda_c}\right)^2 \tag{4}$$

where λ_c is the cut-off wavelength, λ_0 is the free space wavelength, and λ_d is the wavelength in the dielectric filled guide of the cell.

The dielectric loss is determined by bringing the plunger down to the window and minimizing the powder with the probe. Then the plunger is brought up to the various successive minimum positions and the standing wave ratio, ρ, is measured from the width of the minimum. Values of ρ increase for successive minimum settings n. The dielectric loss factor ε'' is approximated by

$$\varepsilon'' = \frac{\lambda_0^2}{\lambda_d} \cdot \frac{2}{\pi\lambda_g} \cdot \frac{\partial(1/\rho_n)}{\partial n} \tag{5}$$

Loss Measurements as Frequency of 48 Gc./sec.—The dielectric constants of solutions at this frequency have been measured by the same principle using an apparatus similar to that described in Fig. 1. The dielectric losses at this frequency are measured by use of the transmission method[6] (see Fig. 3). The dielectric cell is made of an inclined rectangular wave guide with a mica window down (Fig. 4). The power transmitted through the dielectric cell filled with solution is measured and compared with the original power

$$T = \frac{\text{Power transmitted}}{\text{Power received}} = e^{-Sl} \tag{6}$$

5) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 3443 (1950).

6) D. H. Whiffen and H. W. Thompson, *Trans. Faraday Soc.*, **42a**, 114 (1946).

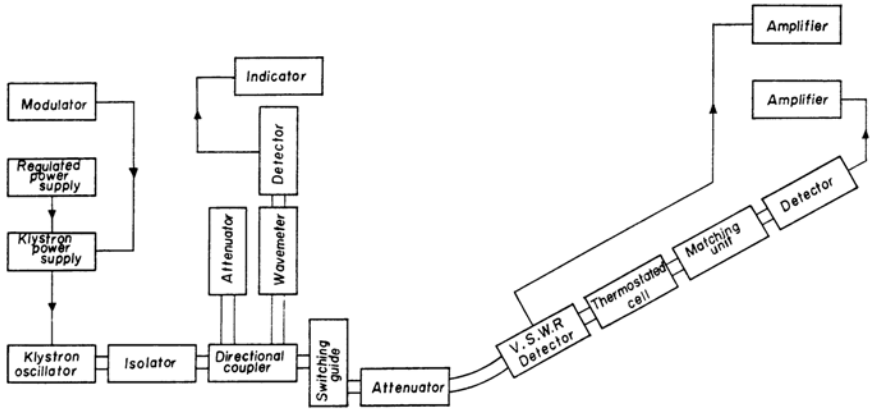


Fig. 3. Block diagram of 48 Gc. apparatus.

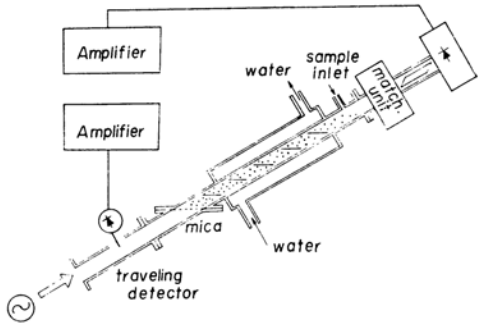


Fig. 4. Dielectric cell for use at 48 Gc.

in which S is defined the attenuation coefficient and l is the depth of the liquid in the cell which can be measured accurately. From values of S the dielectric loss is calculated by

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = S \cdot Q \tag{7}$$

and Q is calculable, e. g., for the H_{10} mode

$$Q = \frac{\beta}{(\pi/a)^2 + \beta^2}$$

where β is the propagation constant $2\pi/\lambda_d$ and a is a constant depending on the dimension of the wave guide. From Eq. 6 one obtains

$$S = \frac{1}{l} \ln\left(\frac{1}{T}\right) \tag{8}$$

In order to eliminate the effects due to the meniscus of the liquid surface and the attenuation of the empty cell the measurements were made varying both the liquid depth and the concentration. By use of the attenuation coefficient, T_0, for the empty cell, values $\ln(T_0/T)$ are considered instead of $\ln(1/T)$ and the difference in $\ln(T_0/T)$ between the solution and the solvent is taken always. From these data one is able to calculate the effective value of S in Eq. 8 from which the desired difference in the $\tan \delta$ values between the solution and the solvent is obtained.

Experimental Materials

Aniline was kept in a cold, dark place with sodium hydroxid for several days and distilled under vacuum-(b. p. 81.0°C at 19 mm., n_D^{20} 1.5860). *p*-Nitroaniline was recrystallized with water and completely dried (m. p. 149.6—149.8°C). These materials were purchased from Wako Pure Chemical Industries (G. R. Grade). *N*, *N'*-Dimethylaniline (b. p. 72.3°C at 9 mmHg., n_D^{20} 1.5585), *N*, *N'*-diethyl aniline (b. p. 89.0°C at 8 mmHg., n_D^{20} 1.5420), 2, 6-dimethylaniline (b. p. 92.0°C at 9 mmHg, n_D^{20} 1.5610) and *N*-methylaniline (b. p. 75.0°C at 8 mmHg, n_D^{20} 1.5704) were distilled under vacuum. These four materials were obtained from Tokyo Kasei Kogyo Co., Ltd.

p-Dioxane was first boiled with HCl and water, then was treated with potassium hydroxide, completely dried with sodium and distilled at 101.4°C. n_D^{20} 1.4224, η 1.2836 cp. and ε'/1 Mc. 2.215 at 20°C. Because of the existence of wall losses ε'' were not measured exactly: estimated values are $\varepsilon'' \simeq$ 0.002/9 Gc., 0.004/24 Gc. and 0.005/48 Gc. Benzene was purified and sistilled in a usual manner at 80.3°C. n_D^{20} 1.5011, η 0.6466 cp. and ε' 2.282 at 20°. Apparent ε'' values were 0.0008/9 Gc., 0.003/24 Gc. and 0.004/48Gc. which are due partly to the wall loss and partly to the trace of water which can only be removed by weeks or months of drying treatment.[7] *n*-Hexane was purified and distilled with sodium at 67.8—68.0°C. n_D^{20} 1.3775, η 0.3238 cp. and ε' 1.9016 at 20°C. All these solvents are of G. R. Grade, Wako Chemical Industries.

Experimental Results

For dilute solutions with small concentration range ($c_2 \leq 0.05$), dielectric constant and loss

7) L. Hartshorn, J. V. L. Parry and L. Essen, *Proc. Phys. Soc.*, **68**, 422 (1955).

TABLE II. SLOPES FOR DEPENDENCE OF DIELECTRIC CONSTANT AND LOSS UPON CONCENTRATION (GRAM FRACTION), AT 20°C

Frequency/sec.	a'	a''
Aniline-Benzene		
1 Mc.	2.93	—
9.33 Gc.	2.65	0.69_7
24.15 Gc.	1.96	0.92_6
48.00 Gc.	1.55	0.82_2
Aniline-Dioxane		
1 Mc.	4.63	—
9.33 Gc.	2.84	1.42
24.15 Gc.	1.80	0.91_6
48.00 Gc.	1.65	0.72_5
Aniline-Hexane		
1 Mc.	2.10	—
9.33 Gc.	2.05_1	0.22_7
24.15 Gc.	1.67_0	0.45_4
48.00 Gc.	1.42	0.46
***N,N'*-Dimethylaniline - Benzene**		
1 Mc.	2.49	—
9.33 Gc.	1.60	0.94
24.15 Gc.	0.83_6	0.67
48.00 Gc.	0.55_6	0.47_6
***N,N'*-Dimethylaniline - Dioxane**		
1 Mc.	3.18	—
9.33 Gc.	1.45	1.07
24.15 Gc.	1.05	0.55_5
48.00 Gc.	0.84	0.37_5
***N,N'*-Diethylaniline - Benzene**		
1 Mc.	2.56	—
9.33 Gc.	0.87	0.94
24.15 Gc.	0.52	0.46
48.00 Gc.	0.40	0.29_2
***N,N'*-Diethylaniline - Dioxane**		
1 Mc.	3.24	—
9.33 Gc.	0.95_5	0.79
24.15 Gc.	0.62_5	0.30_3
48.00 Gc.	0.54	0.24_2
2,6-Dimethylaniline - Benzene		
1 Mc.	2.59	—
9.33 Gc.	2.07	0.80_5
24.15 Gc.	1.24	0.68
48.00 Gc.	0.91	0.58_7
2,6-Dimethylaniline - Dioxane		
1 Mc.	4.02	—
9.33 Gc.	1.88	1.21
24.15 Gc.	1.16	0.64
48.00 Gc.	1.08	0.47_6
***p*-Nitroaniline - Benzene**		
1 Mc.	31.40	—
9.33 Gc.	12.6_7	12.6_7
24.15 Gc.	5.5_7	7.20
48.00 Gc.	3.3_8	4.4_8
***p*-Nitroaniline - Dioxane**		
1 Mc.	43.7	—
9.33 Gc.	4.20	9.5_7
24.15 Gc.	3.0_7	4.72
48.00 Gc.	2.4_3	2.8_9
***N*-Methylaniline - Benzene**		
1 Mc.	3.03	—
9.33 Gc.	1.98	1.01
24.15 Gc.	1.15	0.75
48.00 Gc.	0.89	0.54
***N*-Methylaniline - Dioxane**		
1 Mc.	4.41	—
9.33 Gc.	1.66	1.25
24.15 Gc.	0.92	0.61
48.00 Gc.	0.78	0.41

ε' and ε'' can be expressed as linear functions of concentration.[8]

$$\left.\begin{aligned}\varepsilon' &= \varepsilon_1' + a'c_2 \\ \varepsilon'' &= \varepsilon_1'' + a''c_2\end{aligned}\right\} \quad (9)$$

in which c_2 is the weight fraction of a polar solute and ε_1'' is usually considered zero for a non-polar solvent. The polarity of *p*-dioxane is sometimes in question; two values are reported of either zero of 0.3—0.4 D.[9] The ε_1'' values for benzene and *p*-dioxane are insignificant.

The Debye equation for dilute solutions in a nonpolar solvent is expressed as[10]

$$\frac{a^*-a_\infty}{a_0-a_\infty} = \frac{1}{1+i\omega\tau} \quad (10)$$

in which ω is the angular frequency, τ is the relaxation time, a^* is the complex quantity defined by

$$a^* = a' - ia'' \quad (11)$$

And a_0 and a_∞ are the slopes a' at the static frequency and at the very high frequency, respectively. The equation representing a system with the Cole-Cole distribution of relaxation times is as follows.[10]

$$\frac{a^*-a_\infty}{a_0-a_\infty} = \frac{1}{1+(i\omega\tau_0)^{1-\alpha}} \quad (12)$$

in which τ_0 is the most probable relaxation time and α is the Cole and Cole parameter of distribution.

If the dielectric system under consideration is a

8) K. Higasi and K. Uchiyama, *Bull. Inst. Appl. Elec.*, **17**, 1641 (1965).
9) A. L. McClellan, "Tables of Experimental Dipole Moments," Freemen and Co., San Francisco (1963).
10) K. Higasi, This Bulletin, **39**, 2157 (1966).

TABLE III. AVERAGE RELAXATION TIMES τ_0, DISTRIBUTION CONSTANTS α, AND DIPOLE MOMENTS (20°C)
Units of τ_0: p. sec.

Solute	Solvent	τ_0	Parameter α	Dipole moment (Debye)
Aniline	Benzene	6.7	0	1.50
	Dioxane	19.4	0.0_8	1.75
	Hexane	5.0	0.0_7	1.48
N,N'-Dimethylaniline	Benzene	14.5	0.0_6	1.5_9
	Dioxane	30.4	0	1.6_6
N,N'-Diethylaniline	Benzene	33.2	0	1.81
	Dioxane	47.4	0.1_2	1.89
2,6-Dimethylaniline	Benzene	11.0	0	1.61
	Dioxane	30.1	0.0_8	1.88
p-Nitroaniline	Benzene	24.5	0.0_5	6.2_3
	Dioxane	113.5	0	6.8_4
N-Methylaniline	Benzene	15.0	0.09	1.65
	Dioxane	$33._1$	0.17	1.80

superposition of two independent Debye dispersions, that is, if it has two relaxation times, τ_1 and τ_2, we have the following expression.

$$\frac{a^*-a_\infty}{a_0-a_\infty}=\frac{c_1}{1+i\omega\tau_1}+\frac{c_2}{1+i\omega\tau_2} \tag{13}$$

and

$$c_1+c_2=1 \tag{14}$$

Dielectric data concerning aniline and its derivatives are often examined on the assumption of existence of two relaxation times.[11] Equation 13 might preferably be chosen for this reason if there were no risk of arbitrariness in such an analysis.

In the present paper, however, the usual a' and a'' plot[10,12] based on Eq. 12 is used to obtain τ_0 and α values. This is not to say that the Cole-Cole distribution better represents the actual situation. In fact, the a' and a'' plot is a preliminary step taken in view of a small number of data points, but it well afford a clue for finding an average effect of the dielectric relaxation.

Table II shows the values of two slopes, a' and a'', of six substances obtained in dilute solutions of either benzene or dioxane. By the use of a' and a'' recorded in Table II the a', a'' plot in the complex plane was made for each system and thus the average relaxation time τ_0 and the distribution constant α are obtained (see Table III). Dipole moments are also calculated by the Halverstadt-Kumler approximate equation[13] from the measurements at 1 Mc./sec.

It will be seen at the inspection at Table III that the distribution parameter α is not much different from zero throughout; one would feel that the Debye equations for a single relaxation time may be valid. The Debye equations based on a' and a'' are:[10]

$$\frac{a'-a_\infty}{a_0-a_\infty}=\frac{1}{1+\omega^2\tau^2} \tag{15}$$

$$\frac{a''}{a_0-a_\infty}=\frac{\omega\tau}{1+\omega^2\tau^2} \tag{16}$$

Combination of Eqs. 15 and 16 gives another set of equations:

$$\tau=\frac{1}{\omega}\frac{a_0-a'}{a''} \tag{17}$$

$$\tau=\frac{1}{\omega}\frac{a''}{a'-a_\infty} \tag{18}$$

The values of τ of aniline and 2, 6-dimethylaniline, both in benzene, calculated by use of these equations are recorded in Table IV.

It is interesting to find a gradual decrease of

TABLE IV. RELAXATION TIMES (p. sec.) CALCULATED FROM MEASUREMENTS AT A SINGLE FREQUENCY BY Eqs. 15—18

Equation	Data used	Frequency (Gc./sec.) 9.33	24.15	48.00
Aniline in benzene ($a_\infty=1.07$)				
I (Eq. 15)	$a'a_0\,a_\infty$	7.1_8	6.8_8	5.6_2
II (Eq. 16)	$a''a_0\,a_\infty$	7.6_9	7.2_3	5.5_1
III (Eq. 17)	$a'a''a_0$	6.8_5	6.9_0	5.5_7
IV (Eq. 18)	$a'a''\,a_\infty$	7.5_2	6.8_6	5.6_8
2,6-Dimethylaniline in benzene ($a_\infty=0.80$)				
I (Eq. 15)	$a'a_0\,a_\infty$	10.9_1	11.5_4	12.9_6
II (Eq. 16)	$a''a_0\,a_\infty$	10.6_7	14.3_1	8.8_7
III (Eq. 17)	$a'a''a_0$	11.0_2	13.0_8	9.4_9
IV (Eq. 18)	$a'a''a_\infty$	10.8_1	10.1_9	17.6_9

11) E. L. Grubb and C. P. Smyth, *J. Am. Chem. Soc.*, **83**, 4879 (1961); H. Kramer, *Z. Naturforsch.*, **15a**, 974 (1960); P. Knobloch, ibid., **20a**, 854 (1965).
12) A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 3447 (1950).
13) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

the values of aniline with increase in the frequency; this tendency suggests that there may be another dispersion in the range of higher frequency which the a', a'' plot fails to detect. The observed a'' value at 48 Gc./sec. being too large the a', a'' plot is not satisfactory for 2, 6-diemthylaniline. An examination of τ values in Table IV shows that Eqs. 16 and 17 based on the use of a'' give smaller values of about 9 p. sec. This result is just as expected, however, the use of Eqs. 15 and 18 gives even a higher value than τ_0 11.0 p.sec.*

Discussion

The relaxation times of aniline measured in three solvents increase in the order: hexane 5.0 p.sec., benzene 6.7 p.sec. and dioxane 19.4 p.sec. This trend in τ values is in accordance of the order of viscosities of the solvent, hexane 0.3238 cp., benzene 0.6466 cp., and dioxane 1.2836 cp. which are approximately in the ratio of 1 : 2 : 4. It may be noticed, however, that the change of viscosity from hexane to benzene does not produce much change in relaxation time while its further change to *p*-dioxane resulted in a significant increase.

The effects of viscosity on the relaxation time have been studied in great detail,[14] and it has been confirmed that they are not usually so great as expected from Eq. 3. The observed increase of τ values from hexane to benzene may be regarded as normal.** On the contrary the appreciable increase of τ in dioxane may be considered anomalous, that is, this is an indication, one may infer, that there exists some other factor than the viscosity effect which contributes to the large value of aniline in dioxane.***

In order to examine the above point in more detail the ratio of the relaxation time τ_D obtained in dioxane to that of τ_B in benzene is calculated for six substances (A, B, C, D, E and F) and the result is shown in Table V.

It will be seen that the lowest τ_D/τ_B values are found in *N, N'*-dimethylaniline (B) and *N, N'*-diethylaniline (C). In these molecules two hydrogen atoms of the NH_2 group in aniline are replaced by two methyl or two ethyl radicals, both being inactive in the hydrogen-bonding effect.

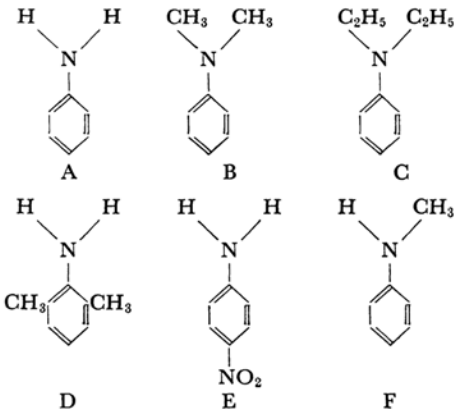
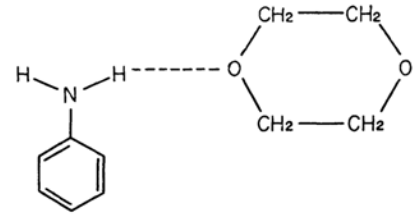


Table V. Ratios of relaxation times, differences of dipole moments and interaction energies

Substance	τ_D/τ_B	$\mu_D-\mu_B$	ΔF^* cal./mol.
Aniline (A)	2.90	0.25	640
N, N'-Dimethylaniline (B)	2.10	0.07	430
N, N'-Diethylaniline (C)	1.43	0.08	210
2,6-Dimethylaniline (D)	2.74	0.27	590
p-Nitroaniline (E)	4.63	0.61	900
N-Methylaniline (F)	2.21	0.15	460

In *N*-methylaniline (F) one finds the ratio τ_D/τ_B to be intermediate between that of aniline (A) and those of *N, N'*-disubstituted anilines (B and C). These results seem to indicate the formation of bonds between amino-hydrogen atoms in aniline and an oxygen atom of the dioxane molecule which leads to a high relaxation time in dioxane.



(I)

The hydrogen bond between the solute and the solvent becomes stronger with an increase in the electropositive nature of the aminohydrogen atoms. Indeed, this occurs in *p*-nitroaniline (E), because the molecule has a considerable contribution from the resonance structure II which has the formal positive unit charge at the nitrogen atom of the amino group.[15] Consequently the hydrogen

* The values a_∞ used in the above estimation of τ are obtained from intercepts of the a', a'' plot (Fig. 5)—it should be noted that a proper choice of a_∞ is very important in this calculation. See K. Higasi and O. Kiyohara, *Bull. Inst. Appl. Elec.*, **19**, 24 (1966).

** This statement is only approximately true, because interaction between solute and benzene is sometimes appreciable.

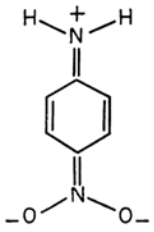
*** The hydrogen bonding of aniline has been studied by several workers, e. g., from ultraviolet study, J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **38**, 896 (1960); H. Baba, Private communication; By N. M. R., B. N. Rao et al., ibid., **40**, 963 (1962), and by dipole moment see Refs. 16 and 17.

14) See, for instance, K. Chitoku and K. Higasi, This Bulletin, **36**, 1064 (1963); K. Higasi, "Dipole Molecules and Chemistry," Hokkaido University, Sapporo (1965), Chapter 1; Krishnaji and A. Mansingh, *J. Chem. Phys.*, **42**, 2503 (1965).

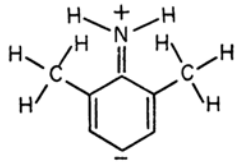
15) Y. Tsuzuki and K. Higasi, *Sci. Papers Inst. Phys. Chem. Res.*, **39**, 185 (1941).

bonding with dioxane is much stronger, producing the highest ratio of τ_D/τ_B for E in Table V.

Contrary to this the resonance structure III for D is less stabilized because of the steric effect of methyl groups. A slightly smaller ratio τ_D/τ_B for 2,6-dimethylaniline than that of aniline may be accounted for by this reason. To sum up, one would expect from the tendency of hydrogen bonding that the ratio τ_D/τ_B will have the order E>A>D>F>B≃C, while the observed order is: E>A>D>F>B>C, in good accord with the anticipation.



(II)



(III)

In Table V the differences between the dipole moments of the same substances measured in dioxane and benzene are recorded. It will be seen that the differences, $\mu_D-\mu_B$, has the order E>A≃D>F>B≃C again in fair agreement with the observed order of τ_D/τ_B. The values $\Delta\mu=\mu_D-\mu_B$ obtained by Smith and his co-workers[16] are E 0.62D>A 0.24D>F 0.18D>B 0.06D again in good agreement with the corresponding values in Table V.

The dipole moments of the 1 : 1 complex of aniline-dioxane is estimated as about 1.88D.[17] On forming a hydrogen bond between aniline and dioxane the apparent dipole moment increases on account of the electron migration effect from the benzene nucleus toward the amino group.[16] And this migration is most pronounced in *p*-nitroaniline (E), next in aniline (A) or in 2, 6-dimethylaniline (D) and then in *N*-methylaniline (F) while no such migration is possible in the remaining substances (B and C).

Next we shall turn to a question what we can conclude from this study on the binding energy of the hydrogen bond between the solute and solvent. By the use of Eq. 2 the value $(\Delta F_2^*-\Delta F_1^*)=\Delta\Delta F^*$ is obtained from τ_D/τ_B—this would represent $\Delta\Delta H^*\simeq\Delta H_2^*-\Delta H_1^*$ if $\Delta S_1^*\simeq\Delta S_2^*$. For aniline (A) $\Delta\Delta F^*$ amounts to 640 cal./mol. which must be associated with both the hydrogen bonding and the viscosity effects. If the latter effect is estimated as about 300 cal./mol., (an average of $\Delta\Delta F^*$ values for two non-hydrogen-bonding substances, B and C) the remaining value 340 cal./mol. may be regarded as arising chiefly from the hydrogen-bonding interaction between the solute and solvent molecules. The same estimation is made for other molecules with the result:

E 600 cal./mol.>A 340 cal./mol.>

D 290 cal./mol.>F 160 cal./mol.

The system of aniline and *p*-dioxane was studied by Few and Smith[17] by the polarization method. According to their estimate about 65% of the aniline is in the form of 1 : 1 complex with dioxane at infinite dilution in dioxane. The measured value $\Delta\Delta F^*$ is associated with the equilibrium mixture; and the energy difference for the complex $\Delta\Delta F^*$ (or possibly $\Delta\Delta H^*$) would be of the order of about 500 cal./mol.

Feodosév and Andreeva[18] found the heat of formation of the aniline-dioxane complex as 0.72 kcal./mol. from an isothermal calorimetric measurement of mixing heats. It is of interest to note that these values, $\Delta\Delta F^*$ (or $\Delta\Delta H^*$) and ΔH are of the same magnitude, although they refer to different mechanisms of the same origin. Both ΔF^* and ΔH^* are associated with the activation for dipole rotation[2] and even $\Delta\Delta H^*$ is not equal to ΔH in this sense, because the former is a part of the hydrogen-bonding energy effective in hindering the dipole rotation.

In Table VI the slopes a_0, a_∞ and a_D are recorded. The a_0 and a_∞ values, which are defined as the slopes a' at the static field and at the very high frequency, respectively, are obtained from the two intercepts of the semi-circles of the a', a'' plot with the abscissa in the complex plane (Fig. 5). The a_D values are obtained from refractivity measurements of dilute solutions and are given by $n^2=n_1^2+a_Dc_2$. Compare this equation with Eq. 9.

It will be seen at Table VI that the differences, $a_\infty-a_D$, are fairly large in some substances (A, D, E, etc.) in which they are not so small as expected to be arising from atomic polarizations.

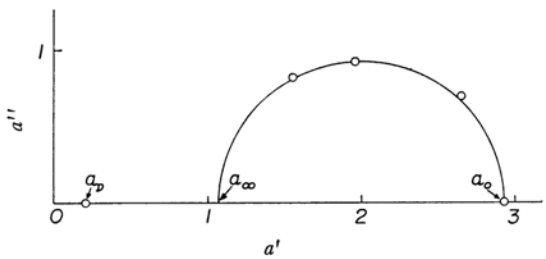


Fig. 5. The a', a'' plot of aniline in benzene.

16) J. W. Smith, "Electric Dipole Moments," Butterworths Sci. Publ., London (1955), p. 313, Table 49. See also C. Curran and G. K. Estok, *J. Am. Chem. Soc.*, **72**, 4575 (1950); K. Kimura and R. Fujishiro, This Bulletin, **32**, 433 (1959).

17) A. V. Few and J. W. Smith, *J. Chem. Soc.*, **1949**, 2781.

18) N. N. Feodosév and T. A. Andreeva, *Chem. Abstr.*, **57**, 144 (1962).

TABLE VI. SLOPES, a_0, a_∞, AND a_D, AND DIFFERENCE $a_\infty - a_D$, CONCENTRATION UNITS BEING THE WEIGHT FRACTION (20°C)

Solute	Solvent	a_0	a_∞	a_D	$a_\infty - a_D$
Aniline (A)	Benzene	2.93	1.07	0.20	0.87
	Dioxane	4.63	1.37	0.49	0.88
N,*N'*-Dimethylaniline (B)	Benzene	2.49	0.41	0.16	0.25
	Dioxane	3.18	0.79	0.40	0.39
N,*N'*-Diethylaniline (C)	Benzene	2.56	0.36	0.10	0.26
	Dioxane	3.24	0.50	0.38	0.12
2,6-Dimethylaniline (D)	Benzene	2.59	0.80	0.14	0.66
	Dioxane	4.02	0.93	0.43	0.50
p-Nitroaniline (E)	Benzene	31.4	2.60	0.67	1.93
	Dioxane	43.7	2.15	0.70	1.45
N-Methylaniline (F)	Benzene	3.03	0.68	0.22	0.46
	Dioxane	4.41	0.62	0.47	0.15

The dipole moment of a polar molecule is approximately given by

$$\mu = B(a_0 - a_D)^{1/2} \tag{19}$$

where

$$B = \frac{1}{2(\varepsilon_1 + 2)} \sqrt{\frac{27 M_2 \boldsymbol{k} T}{\pi \boldsymbol{N} d_1}} \tag{20}$$

when the concentration c_2 is expressed in the units of weight fraction.[19] The symbols M_2, d_1, $\boldsymbol{k}$, T, $\boldsymbol{N}$, etc. have the usual significance.

If the dipole moment associated with τ_0 and α is expressed by μ_0, one may calculate μ_0 by

$$\mu_0 = B(a_0 - a_\infty)^{1/2} \tag{21}$$

and one will find that μ_0 is smaller than μ, sometimes beyond the possible errors. If this difference is anomalously large, we shall suspect whether or not there is another dielectric absorption in the region of the higher frequency. Should such an extra absorption exist, the extra component of the molecular dipole moment would be estimated by

$$\mu^2_{\text{extra}} = \mu^2 - \mu_0^2 = B^2(a_\infty - a_D) \tag{22}$$

The value B of aniline in benzene is about 1.0D at room temperature and hence, μ_{extra} amounts to 0.9D. Caution must be taken if we find a large difference, $a_\infty - a_D$; this point is very important requiring for more detailed analysis. For instance. aniline is believed to have an absorption in the region of a very short wavelength of about 1 mm.[20]; and also from the present measurement at 48 Gc./sec. a very small value of about 1 p.sec. for aniline in benzene is calculated by use of $a_D = 0.20$ and Eq. 16. More experimental data in the millimetre wave region are desirable to characterize the dispersion of a very small relaxation time.

The present work has dealt with the "probable" relaxation time in the main dispersion region and found that this relaxation time becomes much larger when a hydrogen bond is formed between the solute and solvent molecules.

Thanks are due to Professor Hiroaki Baba for helpful discussion and Mr. Kiyoshi Uchiyama for measurements of static dielectric constant, density and refractive index.

19) K. Higasi, *Bull. Inst. Appl. Elec.*, **4**, 231 (1952); *Bull. Inst. Phys. Chem. Res.*, **22**, 865 (1943).

20) C. P. Smyth, Private communications. See also Ref. 11, P. Knobloch who gives $\mu_{\text{extra}} \simeq \mu_2 = 0.9$D with $\tau_2 = 0.5$ p.sec. by use of a_D.