BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2307—2312 (1970)

Dielectric Relaxation and Molecular Structure. I. Dielectric Relaxation in Substituted Anilines

K. K. SRIVASTAVA and J. K. VIJ*[1]

Department of Physics, Panjab University, Chandigarh, India

(Received December 10, 1969)

Measurements of static dielectric constant at 1 Mc, refractive index (for sodium D-line) and complex dielectric constant at 9.44 GHz (X-band) have been made to determine the relaxation times and dipole moments of *N,N′*-dimethylaniline (A), *N,N′*-diethylaniline (B), *o*-chloroaniline (C), *m*-chloroaniline (D) and *p*-chloroaniline (E) in dilute solutions of non-polar solvents. Substances A, B, C and D have been studied in *n*-heptane, benzene decalin and Nujol. The measurements for A and B have also been extended to cyclohexane, whereas E has only been studied in benzene. The values of relaxation time, calculated by Higasi's equations in terms of a_0, a', a'' and a_∞, and those of α, calculated from Cole-Cole's equation in terms of the same parameters, showed an evidence for the existence of more than one relaxation mechanism. This has been interpreted in terms of the intramolecular rotations of the amino (or the substituted amino) group occurring simultaneously with the overall molecular orientation.

A study of dipole moment and dielectric relaxation time has provided an evidence for the existence of internal or intramolecular rotations in several organic molecules.[1-3] The present work extends this study to several substituted anilines. Garg and Smyth[4] have studied liquid aniline and *N,N′*-dimethylaniline. They have analyzed their data with the help of Roberti and Smyth's[5] equation in terms of τ_1 and τ_2 which are 22.0 ps (1 ps $=10^{-12}$ sec) and 0.9 ps for aniline and 28.0 ps and 1.5 ps for dimethylaniline. The values of τ_1 and τ_2 refer to the molecular and intramolecular rotations, respectively. Smyth[6] has postulated that unusually small values of τ_2, obtained for aniline, and a small change in the value of τ_2 from aniline to dimethylaniline, can only be explained by an inversion mechanism for an amino or substituted amino group. In order to confirm his viewpoint, a systematic study of some substituted anilines has been undertaken in various solvents of different viscosity. Chitoku and Higasi[7] have recently studied a few substituted anilines in dilute solutions of benzene and dioxane. They have reported relaxation times in the main dispersion region and have predicted another dispersion region in the mm wave range.

Experimental

Purification of Materials. *Benzene* was purified by the process already described.[8]

n-Heptane (E. Merck quality) was fractionally distilled and the middle fraction was collected. It was then dried over sodium and subsequently distilled (bp 98.0°C).

Cyclohexane (L.R., B.D.H.) was treated like *n*-heptane and the final sample was collected for use (bp 80.0°C).

Decalin (Reidel, Pure grade) was used without purification.

Nujol (B. P. Grade, meant for medicinal purposes) was passed through oil-free sodium wire and was subsequently subjected to vacuum for several hours.

p-Chloroaniline (Fluka A. G., A. R. grade) was used without purification. The following chemicals were imported from Dr. Theodor Schuchardt, West Germany.

N,N′-Dimethylaniline. Analytical reagent, free from monomethylaniline.

N,N′-Diethylaniline. Pure grade.

o-Chloroaniline. Analytical reagent.

m-Chloroaniline. Analytical reagent.

Since the measured values of their physical constants tallied well with literature values, further purification was not deemed necessary.

Table 1 gives a comparative statement of the measured and literature values of physical constants which indicates

---

[*1] Present address: Department of Physics, Punjabi University, Patiala, India.

1) I.d' Or and J. Henrion, *Physik. Z.*, **38**, 426 (1937); E. Fischer and F. C. Frank, *ibid.*, **40**, 345 (1939).

2) K. Higasi and C. P. Smyth, *J. Amer. Chem. Soc.*, **82**, 4759 (1960).

3) W. E. Vaughan and C. P. Smyth, *J. Phys. Chem.*, **65**, 98 (1961).

4) S. K. Garg and C. P. Smyth, unpublished work. (This work has been quoted in the Chemical Society Publication, "Molecular Relaxation Processes) No. 20, (1966), p. 8.

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

6) C. P. Smyth, "Molecular Relaxation Processes," Chemical Society Publication, No. 20 (1966), p. 8.

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

8) J. K. Vij and K. K. Srivastava, *Indian J. Pure Appl. Phys.*, **7**, 391 (1969).

TABLE 1. MEASURED AND LITERATURE VALUES OF DENSITY, VISCOSITY, REFRACTIVE INDEX (Na-D line) FOR ALL THE SOLVENTS AND LIQUID SOLUTES

Substance	Measured values			Literature values		
	25°C d (g/cc)	25°C η (cp)	25°C n_D	25°C d (g/cc)	25°C η (cp)	25°C n_D
Benzene	0.87369	0.600	1.4979	0.87368a)	0.599a)	1.4980a)
n-Heptane	0.68015	0.408	1.3851	0.67963a)	0.388a)	1.3852a)
Cyclohexane	0.77375	0.878	1.4237	0.77389a)	0.886b)	1.4236a)
Decalin	0.87366	2.208	1.4701	—	—	—
Nujol	0.87698	1.476	1.4800	—	—	—
Dimethylaniline	0.95343	1.378	1.5560	0.95198a)	1.159a)/30°C	1.5562a)/24.6°C
Diethylaniline	0.93008	1.938	1.5392	0.9348a)/20°C	3.251a)/11°C	1.54105a)/22.3°C
o-Chloroaniline	—	—	1.5832/30°C	1.21253c)/20°C	—	1.5895c)/20°C
m-Chloroaniline	—	—	1.5895/30°C	1.2225b)15°C	—	1.5930c)/20°C

a) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Press, New York (1950).

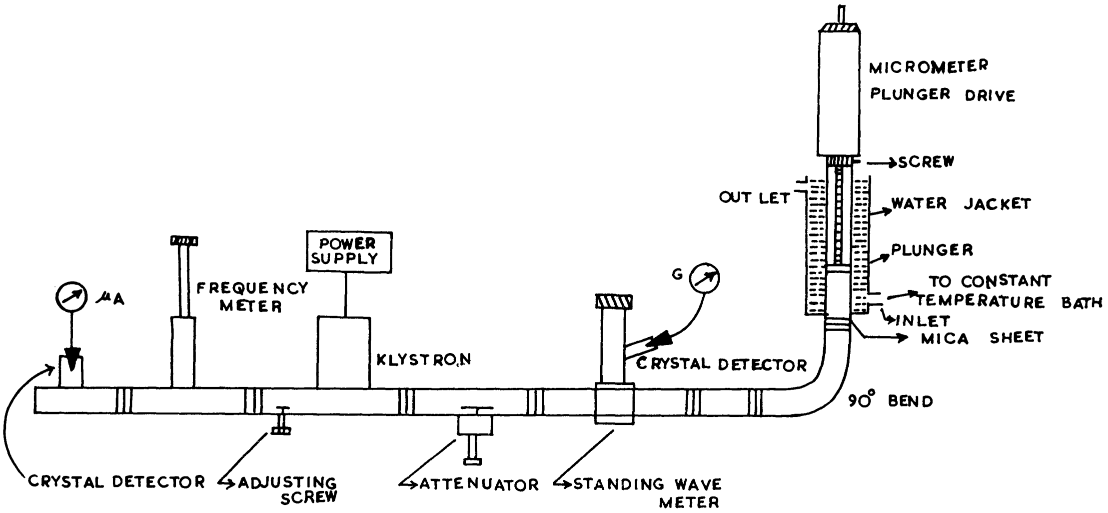
b) *Ibid*, Vol. 2, 1965.

c) J. R. A. Pollack and R. Stevens,"Dictionary of Organic Chemistry," Vol. 2, The Chancer Press Ltd., Bongay, Suffolk, Great Britain (1965), p. 595.

the extent of their purity. The melting point of *p*-chloroaniline (70°C) agreed well with the literature value (70—71°C).

Apparatus and Theory of Measurements. Dielectric constants and losses have been measured at two frequencies (1 Mc and 9.44 GHz). The measurements at 1 Mc are based on the principle of heterodyne beat method using a dielectrometer.9) The accuracy in dielectric constant measurements is estimated to be ±0.05%. Refractive index measurements were made by means of an Abbey Refractometer (Hilger) having an accuracy upto the fourth decimal place. Viscosities were measured by means of a Ubbelohde10) viscometer (accuracy ±0.5%). The final value was computed by applying kinetic energy corrections. Density was measured with an Oswald pycnometer (bulb capacity≈23 cc) having an accuracy of $\pm 5 \times 10^{-5}$ in 1. The temperature of the thermostatic bath was kept constant by means of a Thermomix within ±0.03°C.

Figure 1 shows the block diagram of the 9.44 GHz apparatus imported from Microwave Instruments, England. The measurement technique is based on the standing wave method, developed by Heston, Franklin and Smyth.11)



Set-up in X-band

Fig. 1

---

9) J. K. Vij and K. K. Srivastava, *ibid.*, **7**, 394 (1969).

10) L. Ubbelohde, *Ind. Eng. Chem., Anal. Ed.*, **9**, 85 (1937).

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

With the standing wave detector (SWD) at any fixed position the plunger is turned away from the mica window in the upward direction. The output of the SWD (probe position fixed) is noted at successive minima positions. The distance between the successive minima is equal to $\lambda_2/2$. The positions of at least five minima were noted and their mean value is taken as $\lambda_2/2$. In the majority of the cases, various distances between successive minima do not differ by a factor greater than the least count of the micrometer (0.001 cm). For low-loss materials the dielectric constant is given by

$$\varepsilon' \approx (\lambda_0/\lambda_c)^2 + (\lambda_0/\lambda_2)^2 \tag{1}$$

where λ_c is the cut-off wavelength, λ_0 is the free space wavelength and λ_2 is the wavelength in the dielectric filled guide of the cell.

The dielectric loss is determined by bringing the plunger down to the mica window so that the liquid length is zero. The plunger is then kept at different positions in steps of $\lambda_2/2$ and the standing wave pattern is recorded. The width at "twice minimum power points" is determined in each case and the values of the inverse voltage standing wave ratio ρ are calculated. These values of ρ are then plotted against 'n', *i. e.* the number of half wavelengths from the mica window, and the slope $(\mathrm{d}\rho_{\mathrm{measured}}/\mathrm{d}n)$ is determined for each solution. The dielectric loss factor is approximated by

$$\varepsilon'' \approx (2/\pi)(\lambda_0/\lambda_2)^2(\lambda_g/\lambda_2)(\mathrm{d}\rho_{\mathrm{measured}}/\mathrm{d}n)$$

where λ_g is the empty guide wavelength. The overall estimated accuracy of measurements is 0.5 to 1% for ε' and 2 to 4% for ε''.

For dilute solutions in non-polar solvents, ε, ε', ε'' and ε_∞ can be expressed as linear functions of concentration[12–14] in the following manner:

$$\left.\begin{aligned} \varepsilon &= \varepsilon_1 + a_0 w_2 \\ \varepsilon' &= \varepsilon_1' + a' w_2 \\ \varepsilon'' &= a'' w_2 \\ \varepsilon_\infty &= \varepsilon_{1\infty} + a_\infty w_2 \end{aligned}\right| \tag{3}$$

Subscript 1 refers to the pure solvent, 2 to the solute and subscript ∞ refers to the values at infinite frequency, w_2 may be taken as the weight fraction of the solute. The values of the so called slopes, *i. e.*, a_0, a', a'' and a_∞ for all the systems are given in Table 2. Most of the solutes were studied upto 0.10 weight fraction and the variable parameters were found to vary linearly with concentration. Higasi[14] showed that the Cole-Cole[15] equation can be represented in terms of the slopes a_0, a', a'' and a_∞ which would take the form

$$a' - ja'' = a_\infty + \frac{a_0 - a_\infty}{(1 + j\omega\tau)^{1-\alpha}} \tag{4}$$

TABLE 2. VALUES OF a_0 (SLOPE OF ε *vs.* CONCN. CURVE), a' (SLOPE OF ε' *vs.* CONCN. CURVE), a'' (SLOPN OF ε'' *vs.* CONCN. CURVE) AND a_D (SLOPE OF n_D^2 *vs.* CONCN. CURVE)

Solvent	a_0	a'	a''	a_D
	N,N'-Dimethylaniline			
n-Heptane	1.98	1.51	0.80	0.352
Benzene	2.54_5	1.76	0.98	0.160
Cyclohexane	2.17	1.29	0.64	0.276
Decalin	2.18	1.28	0.58	0.212
Nujol	2.10	0.78	0.23	0.170
	N,N'-Diethylaniline			
n-Heptane	2.00	1.14	0.92	0.325
Benzene	2.46	0.88	0.81	0.104
Cyclohexane	2.22	0.70	0.56	0.276
Decalin	2.51	0.67	0.42	0.189
Nujol	2.47	0.48	0.19	0.132
	o-Chloroaniline			
n-Heptane	2.18	2.14	0.35	0.320
Benzene	3.14	2.80	0.88	0.106
Decalin	3.00	2.22	0.74	0.187
Nujol	2.67	1.75	0.66	0.215
	m-Chloroaniline			
n-Heptance	4.27	3.54	1.08	0.324
Benzene	6.25	4.44	2.33	0.220
Decalin	5.60	3.05	1.54	0.230
Nujol	5.22	2.34	0.93	0.159
	p-Chloroaniline			
Benzene	7.96	4.90	2.49	0.256

τ in this equation is the most probable relaxation time and α is the distribution parameter. For a system with a single relaxation time, α is zero and Eq. (4) becomes Debye's equation in terms of a', a'', *etc.*, *i. e.*

$$a' - ja'' = a_\infty + \frac{a_0 - a_\infty}{1 + j\omega\tau}$$

This equation leads to the following four relations.

$$\frac{a' - a_\infty}{a_0 - a_\infty} = \frac{1}{1 + \omega^2\tau^2} \tag{5}$$

$$\frac{a''}{a_0 - a_\infty} = \frac{\omega\tau}{1 + \omega^2\tau^2} \tag{6}$$

$$a' = a_\infty + \frac{1}{\tau}(a''/\omega) \tag{7}$$

and

$$a' = a_0 - \tau(\omega a'') \tag{8}$$

If the Debye equation for a single relaxation time is valid for the system under consideration and if the measurements are conducted with sufficient accuracy, determination of the correct value of the relaxation time could be made by means of any of the equations mentioned above. Higasi and Kiyohara,[16] in their investigation of Smyth's experimental data, compared the τ values obtained by this method and those by the

---

12) A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3447 (1950).

13) W. F. Hasel, M. D. Magee, S. W. Tucker and S. Walker, *Tetrahedron*, **20**, 2137 (1964).

14) K. Higasi, This Bulletin, **39**, 2157 (1966).

15) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

16) K. Higasi and O. Kiyohara, *Oyo-Denki Kenkyusho Iho*, **18**, 24 (1966).

Table 3. Values of relaxation time, a_∞, a_D, dipole moment and distribution parameter

Solvent	τ(ps)	a_∞	a_D	$(a_\infty - a_D)$	μ(D)	α
N,N′-Dimethylaniline						
n-Heptane	9.1	0.02	0.35	−0.32	1.61	$\leqslant 0$
Benzene	13.4	0.57	0.16	0.41	1.59	0.11
Cyclohexane	23.2	0.83	0.28	0.55	1.60	0.24
Decalin	26.1	0.91	0.21	0.70	1.49	0.32
Nujol	96.7	0.74	0.17	0.57	1.46	0.66
N,N′-Diethylaniline						
n-Heptane	15.8	0.06	0.32	−0.26	1.82	≤ 0
Benzene	32.9	0.47	0.19	0.28	1.76	0.15
Cyclohexane	45.7	0.49	0.28	0.21	1.80	0.18
Decalin	73.8	0.57	0.19	0.38	1.80	0.44
Nujol	176.6	0.46	0.13	0.33	1.79	0.62
o-Chloroaniline						
n-Heptane	2.4	−1.32	0.32	−1.64	1.80	0
Benzene	6.5	0.52	0.11	0.41	1.88	0.03
Decalin	17.7	1.51	0.19	1.32	1.86	0.30
Nujol	23.4	1.28	0.22	1.06	1.71	0.33
m-Chloroaniline						
n-Heptane	11.3	1.95	0.32	1.63	2.67	0.16
Benzene	13.0	1.42	0.22	1.20	2.67	0.10
Decalin	27.8	2.12	0.23	1.89	2.60	0.34
Nujol	51.9	2.04	0.16	1.88	2.49	0.53
p-Chloroaniline						
Benzene	20.6	2.88	0.26	2.62	3.02	0.25

usual method of Cole-Cole[15] for three different cases. The important conclusion drawn was the dependence of relaxation time upon the choice of a_∞.

In case the system has a distribution of relaxation times, values of τ and α can be calculated from the measurement of a' and a'' at a single frequency[14,17] by using the equations.

$$\tau = \frac{1}{\omega}\left(\frac{A^2+B^2}{C^2}\right)^{1/2(1-\alpha)} \tag{9}$$

and

$$1-\alpha = \left(\frac{2}{\pi}\right)\tan^{-1}\frac{A}{B} \tag{10}$$

where

$$\left.\begin{aligned} A &= a''\,(a_0 - a_\infty) \\ B &= (a_0 - a')(a' - a_\infty) - a''^2 \\ C &= (a' - a_\infty)^2 + a''^2 \end{aligned}\right| \tag{11}$$

Though this method has not been used by many workers yet the authors feel that it can provide more information, particularly for non-rigid molecules, in the absence of data at various frequencies. This method can, at least, determine the degree of distribution of various relaxation processes.

Method Adopted for the Calculation of Relaxation Time. If a system possesses a single relaxation time, then the values of τ calculated by using either of the four equations ((5) to (8)), should be the same within experimental errors, because all these relations are basically derived from a single equation. In the absence of an exact knowledge of a_∞, values of τ should preferably be calculated by using Eq. (8). Knowing τ for such a system, the value of a_∞ can subsequently be computed by the use of Eq. (7). This value of a_∞ should be slightly higher than the corresponding a_D value of the system, because a_∞ term involves some contribution from atomic polarization as well.

Even if the system possesses two relaxation times sufficiently far apart, values of τ can be calculated by using Eq. (8) and consequently the values of a_∞ can be estimated. Then the difference $(a_\infty - a_D)$ would give us an idea about the dispersion range to which the τ value belongs. With this picture in mind, the values of τ have been calculated for all the molecules in different solvents and these values are presented in Table 3 which also contains a_∞ values. The experimentally determined values of a_D have also been inserted in this table with a view to estimate the magnitude of $(a_\infty - a_D)$.

Discussion

A perusal of Table 3 reveals that there is a regular increase in the relaxation times of all the molecules as the solvent viscosity increases. Another noteworthy feature is the unusually high values of $(a_\infty - a_D)$ which should be negligibly small if the

---

[17] G. L. Clark, *J. Chem. Phys.*, **25**, 125 (1956).

system has a single relaxation time. The large difference suggests that apart from relaxation in the main dispersion region, another relaxation mechanism seems to occur in the mm range which is due to the relaxation of the amino (or the substituted amino) group. One would therefore conclude that the relaxation process in anilines involves the molecular rotation as well as the intramolecular rotational mechanism. Also, it is interesting to note that the a_∞ values for all the anilines (except *m*-chloroaniline) are either less than the a_D values or negative in *n*-heptane. The values of relaxation time are also found to be relatively less in this solvent. This indicates that in *n*-heptane (having the lowest viscosity coefficient), there is a little disparity between the values of relaxation time for both processes which jointly contribute to the observed loss by competing with each other. The intramolecular process may possibly dominate.

We conclude that these relaxation times correspond to the ones in the main dispersion region.

Grubb and Smyth[18] have studied pure dimethylaniline and predicted, with reservation, two relaxation mechanisms with slightly hindered rotations of $N(CH_3)_2$ group. One of us (K.K.S.) also made a dielectric relaxation study[19] of liquid *N,N'*-dimethylaniline and *N,N'*-diethylaniline using two microwave frequencies (9.72 GHz) and 31.82 GHz), and analyzed the data with the help of "Cole-Cole plots" by taking ε_∞ as the square of refractive index. The findings show that the most probable relaxation time (τ) in both cases is frequency-dependent. The values obtained for the molecular relaxation time at 9.72 GHz are 38.2 ps for dimethylaniline and 290.3 ps for diethylaniline, whereas for 31.82 GHz, these values are 84.7 ps and 167.1 ps respectively. Furthermore, K.K.S. also found high values of distribution parameter (α), *i.e.*, 0.59 for dimethylaniline and 0.52 for diethylaniline. All these reported values correspond to the measurements at 30°C.

These observations and an examination of ($a_\infty - a_D$) values (given in Table 3) provide evidence of two relaxation mechanisms in anilines. One involves the rotation of the molecule as a whole and the other involves intramolecular or the group rotation. This suggests that the dipole in anilines is inclined at a particular angle to the C–N bond, thus making the molecule nonplaner. This possibly leads to the conclusion that the conjugation energy is insufficient to make the molecule planer. The conclusion supports the one already drawn by Tiganik[20] from the dipole moment studies. The amino group together with the benzene ring perhaps retains its pyramidal shape similar to that of an ammonia molecule even when one of its hydrogen atoms has been replaced.

Distribution Parameter (α) and Dipole Moment. In the absence of experimental data for a wide range of frequencies, the Cole-Cole[16] equation has been used in the form of relations (10—11) for the calculations of the distribution parameter (α) with the assumption that $a_\infty \approx a_D$. This will at least provide us with qualitative information about the existence of more than one relaxation mechanism. The values of relaxation time have purposely not been calculated by this method as it will give values in agreement with the values given in Table 3 only for the cases having $\alpha \approx 0$.

These values of distribution parameter are listed in Table 3 which also contains the dipole moments calculated by using the modified Higasi's equation.[8]

Study of Relaxation Time, Distribution Parameter and Dipole Moment Values. *a) N,N'-Dimethylaniline and N,N'-Diethylaniline.* Table 3 shows that for both these substances, relaxation time values increase with the increasing viscosity of the medium. Their reported[7] values in benzene are 14.5 ps and 33.2 ps at 20°C, whereas the authors found them to be 13.4 ps and 32.9 ps at 25°C. Obviously, the agreement between the two is good. Again the value of τ for dimethylaniline in benzne, determined by Kramer,[21] is 13.7 ps again in good agreement with the present value.

The reported[7] values of distribution parameter for dimethylaniline and diethylaniline in benzene, obtained by "Cole-Cole Plots", are 0.06 and 0.0 respectively as against 0.11 and 0.15 obtained by the authors. Certainly, the disparity is due to a different method adopted for calculations. The present method provides, at least qualitatively, a direct evidence of the existence of more than one relaxation mechanism, because the α values show a systematic increase with the increase in viscosity of the medium and are, in general, unusually high. Such large values cannot merely be due to the distribution of activation energies. It certainly indicates that there is more than one relaxation mechanism and that the disparity between the values of relaxation time increases with viscosity. However in *n*-heptane, α values for both these substances are slightly less than zero which perhaps indicates the predominance of intramolecular relaxation process in this solvent. These predictions are in agreement with those already drawn from the negative values of ($a_\infty - a_D$).

Small variations in the dipole moment values for different solvents are possibly due to the solvent effect.

b) o-, m-, and p-Chloroanilines. Liquid *o*- and *m*-chloroanilines have also been studied by Bhattacharyya[22] at a wavelength of 3.18 cm. His

---

[18] E. L. Grubb and C. P. Smyth, *J. Amer. Chem. Soc.*, **83**, 4879 (1961).

[19] K. K. Srivastava, *J. Phys. Chem.*, **74**, 152 (1970).

[20] L. Tiganik, *Z. Physik. Chem.*, **1413**, 135 (1931).

[21] H. Kramer, *Z. Naturforsch.*, **15a**, 66, 974 (1960).

[22] T. J. Bhattacharyya, *Indian J. Phys.*, **36**, 533 (1962).

values of relaxation time, calculated by Debye's equation, are 12.28 ps and 12.49 ps respectively. From the existence of a loss-maxima at 30°C in both cases, he inferred that the amino group is free to rotate and the presence of a chlorine group does not hinder its rotations in any way. It was thought therefore, that the study of the relaxation time in various solvents would give more information about the nature of intramolecular process.

Table 3 again shows a regular increase in relaxation time of these anilines with the increasing viscosity of the solvent. Of course, the variation is not as large as should be expected from Debye's equation[23,24] for a rotating sphere in a continuous fluid of viscosity η. On examining α values, one finds a systematic increase as was the case for dimethyl and diethyl anilines. The increase in values with the increasing viscosity of the medium is interpreted in terms of the disparity in the two relaxation mechanisms involved in the relaxation process. The almost regular rise in α further implies that the molecular relaxation time regularly increases with viscosity, whereas the intramolecular mechanism does not seem to increase very much with the viscosity of the medium. However, one does not expect such behaviour if the amino group (or the substituted one) rotates around the (C–N) bond, because it has some effective volume and this volume goes on increasing with the substitution of the radicals: CH_3 and C_2H_5, *etc.* Amino (or the substituted amino) group possibly relaxes with an inversion mechanism similar to the ammonia molecule, as postulated by Smyth.[6] However, a detailed and systematic study of the substances with a corresponding analysis of the data in terms of τ_1 and τ_2 is required before confirming this possibility. This is not possible with the measurements at two frequencies.

The values of relaxation time for *o*-, *m*- and *p*-isomers measured in benzene at 30°C are 6.5 ps, 13.0 ps and 20.6 ps respectively. These values increase with the shift of chlorine group from *o*- to *m*-, and finally to *p*-position with respect to the amino group. A regular variation in τ values may either be due to the change in the molecular volume or due to a change in the effective length of the dipole involved in the orientation process. The molecular volume (M/d) in all the three cases is approximately the same, *i.e.*, 106 cc. It, therefore, seems that the effective change in length of the dipole is actually responsible for the observed rise in relaxation times of these substituted anilines. Another interesting feature is that the values of α for these anilines in a particular solvent, in general, increase from *o*- to *m*- to *p*-isomers. This indicates, as is expected, that the hindrance for intramolecular rotation of NH_2 group is greater in *o*-chloroaniline, less in *m*-chloroaniline and still less in *p*-chloroaniline.

The authors are grateful to Professor H. S. Hans, Head, Department of Physics, and Professor V. B. Bhanot for their interest in the work and for providing the facilities.

---

[23] P. Debye, "Polar Molecules," Chemical Catalogue, New York (1929); *Trans. Faraday Soc.*, **30**, 679 (1934).

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