# Dielectric Relaxation and Molecular Structure. III. Dielectric Relaxation Study of Some Anilines in Benzene Solutions at Different Temperatures

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Measurements of relative permittivity at 1 MHz and at 9.46 GHz, the refractive index for the Sodium D-line, have been made for (a) *N,N*-dimethylaniline, (b) *N,N*-diethylaniline, (c) *o*-chloroaniline, (d) *m*-chloroaniline and (e) *p*-chloroaniline at temperatures of 15, 25, 35, and 45°C in dilute solutions of benzene. Dielectric relaxation times $\tau(1)$ and $\tau(2)$ have been calculated by the method recently suggested by Higasi, Koga, and Nakamura in terms of the slopes $a_0$, $a'$, $a''$, and $a_D$. It is remarked that $\tau(2)$ at the experimental frequency of 9.46 GHz leads to $\tau_1$, the relaxation time for overall rotation, whereas $\tau(1)$ becomes an explicit function of $\tau_1$ and $\tau_2$. These determinations suggest the presence of both molecular and intramolecular rotations in the molecules. The results for $\tau(2)$ show a systematic decrease with increase in temperature whereas for $\tau(1)$ there seems to be no observable trend. The enthalpy and entropy of activation for molecular dielectric relaxation process has been determined. The enthalpy of activation for (a) and (b) is of the same order of magnitude (*i.e.*, 3 kcal/mol), and the same is true for the case of (d) and (e) (1.8 kcal/mol) but 6.8 kcal/mol for (c). It appears that in *o*-chloroaniline, there is a finite probability of H–Cl bond formation between one of the amino hydrogens and the neighbouring chlorine atom.

This work deals with the dielectric relaxation mechanism of systems with two Debye dispersions. A study on these molecules in different non-polar solvents at various temperatures has been reported.[1] On an examination of the values of $(a_\infty - a_D)$, the authors suggested the possibility of two Debye dispersions in these substances. Chitoku and Higasi[2] studied dimethylaniline in benzene and dioxane solutions at 20°C at three different frequencies in the main dispersion region. Besides giving useful information on the behaviour in two solvents, their results also suggested the presence of two Debye dispersions. Pure dimethylaniline has been studied by Grubb and Smyth,[3] Garg and Smyth[4] and, Srivastava.[5] Though the results differ to some extent, all agree that two dispersions exist in dimethylaniline. Pure diethylaniline was studied by Srivastava.[5] He reported the (Cole–Cole) distribution parameter value to be as high as 0.52/30°C. Recently Tucker and Walker[6] studied *m*- and *p*-chloroanilines at 25°C in dilute solutions of cyclohexane. They gave two dielectric relaxation time values, one for overall dielectric relaxation process and another for intramolecular process. Another remarkable result of their studies is the variation of the weight factor for intramolecular relaxation process with the concentration of the solute.

The present study has two objects. Firstly to get more insight into the nature of dielectric relaxation process, and secondly, since not many molecules of this type have been studied in a non-polar solvent at different temperatures, to get some clue as to their behaviour from the heats of activation for the dielectric relaxation process. For this, the validity of Eyring's equation[7–10] has been taken for granted although its validity is still a matter of debate.

The possibility of getting information on the presence of an intramolecular relaxation mechanism from the data at a single frequency in the dispersion region has been another controversial problem. But recent analysis by Higasi *et al.*,[12] shows that there definitely exists a possibility of estimating either of the two relaxation times. An attempt has therefore been made to use this method for an estimation of the dielectric relaxation time for the overall rotational process. It is pointed out that this method may become an alternative to Bergmann's[13] method for estimating both the dielectric relaxation times, under certain conditions.

## Experimental

The liquids are of purity standards. The measurements for determining the relative permittivity at the temperatures of 15, 25, 35, and 45°C have been made by the same techniques. The values of the slopes are calculated from the experimental plots of the data *vs.* weight fraction.[1]

## Calculations and Results

The Debye equation[14,15] in terms of $a_0$, $a'$, $a''$, and $a_\infty$ yields two independent equations

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$$\tau\,(1)=\frac{a''}{\omega\,(a'-a_\infty)} \tag{1}$$

$$\tau\,(2)=\frac{a_0-a'}{\omega a''} \tag{2}$$

where $a_0$, $a'$, $a''$, and $a_\infty$ are defined in the linear range by the equations:

$$\epsilon=\epsilon_1+a_0\omega_2$$

$$\epsilon'=\epsilon'_1+a'\omega_2$$

$$\epsilon''=a''\omega_2$$

$$\epsilon_\infty=\epsilon_{1\infty}+a_\infty\omega_2$$

Subscript 1 refers to pure solvent, 2 to solute and ∞ to the values at infinite frequency. $\omega_2$ may be taken as weight fraction of the solute. Having defined; $\tau(1)$ and $\tau(2)$ by Eqs. (1) and (2), Higasi, Koga, and Nakamura[12)] have set up the following relations (3) and (4), between $\tau(1)$, $\tau(2)$; $\tau_1$ and $\tau_2$. $\tau_1$ and $\tau_2$ are the dielectric relaxation times for molecular and intramolecular rotations, respectively.

$$\tau(1)=A\tau_2$$

where
$$A=\frac{[m-(m-1)C_2]+mx^2[1+(m-1)C_2]}{1+[1+(m^2-1)C_2]x^2} \tag{3}$$

$$m=\frac{\tau_1}{\tau_2},\ x=\omega\tau_2$$

$$\tau(2)=B\tau_2$$

where
$$B=\frac{m^2-(m^2-1)C_2+m^2x^2}{m-(m-1)C_2+mx^2[1+(m-1)C_2]} \tag{4}$$

At the experimental frequency of 9.46 GHz, the value of $x$ (with the preknowledge of the approximate value of $\tau_2$) is of the order of $10^{-1}$. One can therefore safely neglect 1 in comparison to $m$ without introducing much error.

Equation (4) is therefore reduced to

$$\tau\,(2)=\frac{\tau_1}{\tau_2}\cdot\tau_2=\tau_1 \tag{5}$$

Under similar circumstances, Eq. (3) yields

$$\tau(1)=\tau_1(1-C_2)+C_2\tau_2 \tag{6}$$

This shows that the results given by Eq. (2) in our case would correspond to the dielectric relaxation time for overall rotation and those given by Eq. (1) are the implicit functions of $\tau_1$, $\tau_2$, and $C_2$, the weight factor for intramolecular relaxation mechanism. It should be remarked that since the value given by $\tau(1)$ is a sort of average dielectric relaxation time, $a_\infty$ should be the one corresponding to $a_D$ after a due account for the infrared dispersion ($\Delta a_D$) has been made. In the present calculations, $\Delta a_D$ has been neglected owing to its expected value between 5—10% of $a_D$ which is within the range

TABLE 1. VALUES OF $a_0$ (SLOPE OF $\epsilon$ *vs.* CONCN. CURVE), $a'$ (SLOPE OF $\epsilon'$ *vs.* CONCN. CURVE), $a''$ (SLOPE OF $\epsilon''$ *vs.* CONCN. CURVE) AND $a_D$ (SLOPE OF $n_D{}^2$ *vs.* CONCN. CURVE)

| Temp. (°C) | $a_0$ | $a'$ | $a''$ | $a_D$ | Dielectric Relaxation (Time values in ps) |  | Literature values in ps |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | $\tau(1)$ | $\tau(2)=\tau_1$ | $\tau_0$ | $\tau_1$ | $\tau_2$ |
| *N,N*-Dimethylaniline |  |  |  |  |  |  |  |  |  |
| 15 | 2.65 | 1.73 | 0.90 | 0.15 | 9.6 | 17.2 | 14.5[2)]/20°C<br>(B)[a)] | 28.0[4)]/20°C<br>(L) | 1.5[4)]<br>(L) |
| 25 | 2.54 | 1.88 | 0.87 | 0.17 | 8.6 | 12.8 | 13.7 | 13.4 | — |
| 35 | 2.41 | 1.74 | 0.93 | 0.18 | 10.0 | 12.1 |  |  |  |
| 45 | 2.30 | 1.86 | 0.90 | 0.17 | 9.0 | 8.2 |  |  |  |
| *N,N*-Diethylaniline |  |  |  |  |  |  |  |  |  |
| 15 | 2.70 | 1.07 | 0.84 | 0.11 | 14.4 | 33.7 | 33.2[2)]/20°C |  |  |
| 25 | 2.48 | 1.00 | 0.82 | 0.12 | 15.7 | 30.5 | — | 32.9[1)] |  |
| 35 | 2.27 | 1.16 | 0.76 | 0.13 | 12.4 | 24.6 |  |  |  |
| 45 | 2.08 | 1.24 | 0.73 | 0.14 | 10.6 | 19.4 |  |  |  |
| *o*-Chloroanoiline |  |  |  |  |  |  |  |  |  |
| 15 | 3.70 | 2.85 | 0.94 | 0.14 | 5.7 | 14.9 |  |  |  |
| 25 | 3.43 | 2.80 | 0.90 | 0.19 | 5.7 | 11.5 | — | 6.5[1)]/30°C |  |
| 35 | 3.12 | 2.77 | 0.77 | 0.20 | 4.9 | 7.5 |  |  |  |
| 45 | 2.78 | 2.57 | 0.76 | 0.15 | 5.2 | 4.5 |  |  |  |
| *m*-Chloroaniline |  |  |  |  |  |  |  |  |  |
| 15 | 6.75 | 4.20 | 2.67 | 0.16 | 10.9 | 15.7 |  |  |  |
| 25 | 6.50 | 4.12 | 2.57 | 0.24 | 10.9 | 15.2 | 12.4[6)]<br>(C) | 13.2[6)]<br>(C) | 2[6)]<br>(C) |
| 35 | 6.25 | 4.36 | 2.19 | 0.26 | 8.8 | 14.2 |  | 13.0[1)]/30°C |  |
| 45 | 5.89 | 4.37 | 2.07 | 0.23 | 8.2 | 12.1 |  |  |  |
| *p*-Chloroaniline |  |  |  |  |  |  |  |  |  |
| 15 | 8.70 | 5.68 | 2.81 | 0.16 | 8.5 | 17.6 |  |  |  |
| 25 | 8.20 | 5.57 | 2.85 | 0.24 | 8.8 | 15.2 | 12.4[6)]<br>(C) | 15.3[6)]<br>(C) | 2[6)]<br>(C) |
| 35 | 7.70 | 5.64 | 2.61 | 0.26 | 8.0 | 13.0 |  | 20.6[1)]/30°C |  |
| 45 | 7.10 | 5.37 | 2.66 | 0.23 | 9.1 | 11.9 |  |  |  |

a) The name of the solvent in which the measurements are made is given in brackets.
B=Benzene, L=Pure liquid and C=Cyclohexane, Benzene where not specified. Temperature: 25°C where not specified.

of the accuracies for $a_0$, $a'$, $a''$, and $a_D$.

The determined values of $a_0$, $a'$, $a''$, and $a_D$ at temperatures of 15, 25, 35, and 45°C for the various molecules in benzene solutions are given in Table 1.

Free energy of activation ($\Delta F_\varepsilon$), enthalpy of activation ($\Delta H_\varepsilon$) and entropy of activation for the dielectric relaxation and viscous flow are calculated by using Eyring's equations.[10]

$$\tau = \frac{h}{kT}\exp\frac{\Delta F_\varepsilon}{kT}$$

$$\eta = \frac{hN}{V}\exp\frac{\Delta F_\eta}{kT} \tag{7}$$

where

$$\Delta F_\varepsilon = \Delta H_\varepsilon - T\Delta S_\varepsilon$$

and

$$\Delta F_\eta = \Delta H_\eta - T\Delta S_\eta \tag{8}$$

According to Eqs. (7) and (8), plots of $\log(\tau T)$ *vs.* $1/T$ and $\log(\eta T)$ *vs.* $1/T$ should be straight lines. Their slopes are equal to $\Delta H_\varepsilon/R$ and $\Delta H_\eta/R$, respectively. The plots of $\log(\tau_1 T)$ *vs.* $1/T$ for various substances are given in Figs. 1—5.

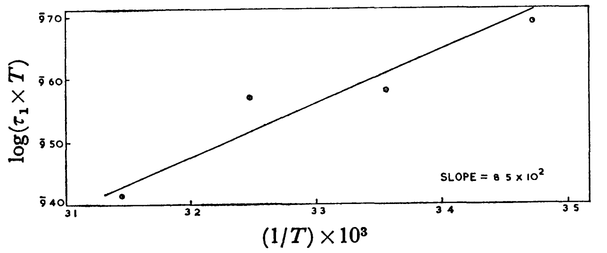

Fig. 1. Dimethylaniline

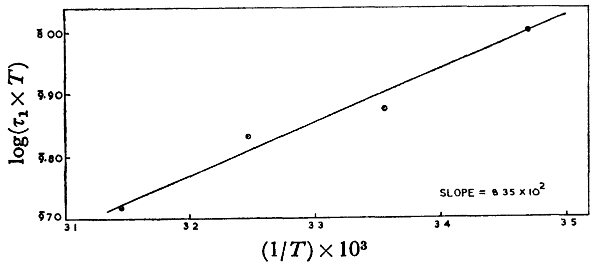

Fig. 2. Diethylaniline.

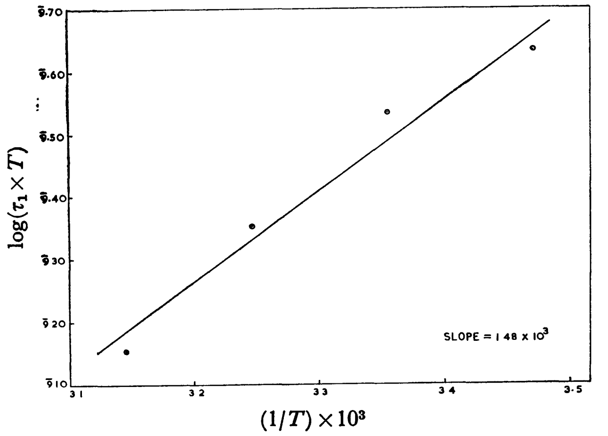

Fig. 3. *o*-Chloroaniline.

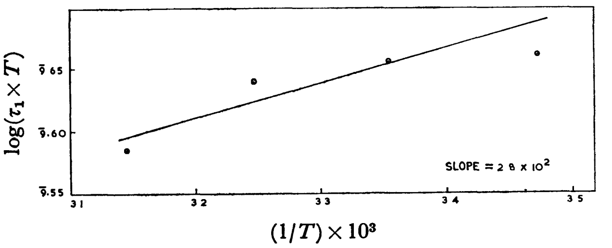

Fig. 4. *m*-Chloroaniline.

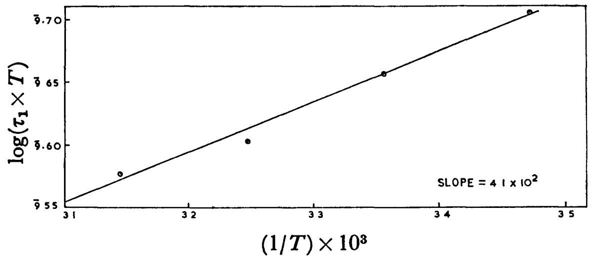

Fig. 5. *p*-Chloroaniline.

TABLE 2. THERMODYNAMIC PARAMETERS

| Temp. (°C) | Free energy of activation kcal/mol | | Enthalpy of activation kcal/mol | | Entropy of activation kcal/mol | |
|---|---|---|---|---|---|---|
| | $\Delta F_\varepsilon$ | $\Delta F_\eta$ | $\Delta H_\varepsilon$ | $\Delta H_\eta$ | $\Delta S_\varepsilon$ | $\Delta S_\eta$ |
| | | *N*,*N*-Dimethylaniline | | | | |
| 15 | 2.66 | 2.89 | | | 4.3 | −1.32 |
| 25 | 2.60 | 2.91 | 3.89 | 2.51 | 4.3 | −1.34 |
| 35 | 2.67 | 2.93 | | | 4.0 | −1.36 |
| 45 | 2.53 | 2.95 | | | 4.3 | −1.38 |
| | | *N*,*N*-Diethylaniline | | | | |
| 15 | 3.04 | 2.89 | | | 0.59 | −1.32 |
| 25 | 3.11 | 2.91 | 3.21 | -do- | 0.33 | −1.34 |
| 35 | 3.10 | 2.93 | | | 0.37 | −1.36 |
| 45 | 3.07 | 2.95 | | | 0.47 | −1.38 |
| | | *o*-Chloroaniline | | | | |
| 15 | 2.58 | 2.89 | | | 14.4 | −1.32 |
| 25 | 2.53 | 2.91 | 6.75 | -do- | 17.5 | −1.34 |
| 35 | 2.37 | 2.93 | | | 14.2 | −1.36 |
| 45 | 2.15 | 2.95 | | | 14.4 | −1.38 |
| | | *m*-Chloroaniline | | | | |
| 15 | 2.60 | 2.89 | | | −4.58 | −1.32 |
| 25 | 2.70 | 2.91 | 1.28 | -do- | −4.80 | −1.34 |
| 35 | 2.77 | 2.93 | | | −4.83 | −1.36 |
| 45 | 2.63 | 2.95 | | | −4.24 | −1.38 |
| | | *p*-Chloroaniline | | | | |
| 15 | 2.67 | 2.89 | | | −2.79 | −1.32 |
| 25 | 2.70 | 2.91 | 1.87 | -do- | −2.78 | −1.34 |
| 35 | 2.71 | 2.93 | | | −2.72 | −1.36 |
| 45 | 2.76 | 2.95 | | | −2.80 | −1.38 |

## Discussion

A perusal of dielectric relaxation time values for the molecules in Table 1 shows that $\tau(1)$ and $\tau(2)$ differ and the difference is beyond the theoretical and experimental errors involved in computing these with the help of Eqs. (1) and (2). An examination of $\tau(2)$ values for all the molecules also shows a systematic decrease with an increase in temperature whereas $\tau(1)$ dose not seem to follow any trend. It might suggest the following:

i) The intra-molecular relaxation mechanism is such that the dielectric relaxation time associated with it does not change much with temperature. It might mean that the amino or substituted amino group relaxes by an inversion mechanism as postulated by Smyth.[16]

ii) The weight factor ($C_2$) for intramolecular relaxation mechanism increases with the increase in temperature such that at a higher temperature the total contribution to $\tau(1)$ according to Eq. (6) increases due to intramolecular rotation term and contribution to $\tau(1)$ decreases due to the remaining term for overall rotation both because of less $(1-C_2)$ value as well as lesser $\tau_1$ value.

These suggestions perhaps can be verified if these types of measurements can be conducted at a few more frequencies particularly in the range of mm wavelength. However, the interpretation of the results might be difficult particularly for the substances like *o*, *m*, and *p*-chloroanilines, in view of the possibility for such molecules to have an intramolecular relaxation time associated with the rotation of the chloro group.[17–20]

N,N-*Dimethylaniline and* N,N-*Diethylaniline.* The values of dielectric relaxation time $\tau_1$ or $\tau_2$ for dimethylaniline and diethylaniline are 12.8 ps and 30.5 ps, respectively, at 25°C. These values show good agreement with those reported[1] from this laboratory *i.e.*, 13.4 ps and 32.9 ps at 25°C. These also show good agreement with even $\tau_0$ values given by Chitoku and Higasi,[2] *i.e.*, 14.5 ps and 33.2 ps respectively at 20°C.

Enthalpy of activation for the two molecules is nearly the same which indicates that both have to overcome almost the same barrier height for overall rotation although the molecular size of diethylaniline might be more comparable to that of dimethylaniline. The entropy of activation for the two molecules is a small positive quantity indicating that the activated system is in a state of slight disorder in comparison to the initial system.

o-*Chloroaniline.* The dielectric relaxation time of overall rotation for *o*-chloroaniline at 25°C is 11.5 ps. This might seem to be small in comparison to the molecular size, but greater than that of the molecule formed by attaching any of the two groups. The reported[17] $\tau$ values for chlorobenzene are 7.4 ps to 9.6 ps. Recently $\tau(1)$ value of 3.9 ps has been reported[17] for this molecule at 20°C from observations at 100 GHz which might lead to some very interesting conclusion for the rigid molecules. For aniline in non-polar solvents, literature[6,17] $\tau$ values vary from 1.2—8.1 ps. The most remarkable observation appears to be the large enthalpy of activation in comparison to that of other molecules of this type. This suggests that at a particular temperature there exsits a finite probability of H–Cl bond formation between one of the amino hydrogens and the neighbouring chlorine atom and this possibility decreases with the increase in temperature. This conclusion supports that already given by Cumper and Singleton[21] from the dipole moment studies.

m- *and* p-*Chloroanilines.* The value of dielectric, relaxation time at 25°C incidentally is 15.2 ps for both the molecules. The value compares favourably well with 13.2 ps and 15.3 ps determined by Tucker and Walker in dilute solutions of cyclohexane for *m*- and *p*-chloroanilines respectively. The enthalpy of activation for both molecules is the same and the order of magnitude is quite less as compared to *o*-chloroaniline. This indicates that both molecules have the same potential barrier and H–Cl type of bond formation as stipulated for *o*-chloroaniline seems improbable. This appears quite acceptable due to the large distance between the amino hydrogens and chloro groups in these molecules.

The literature values of dielectric relaxation time of overall rotation are available only for *m*- and *p*-chloroanilines in dilute solutions of cyclohexane. An agreement with these values suggests that in future $\tau(1)$ and $\tau(2)$ method given by Higasi *et al.* might become a good alternative method for finding the dielectric relaxation times. Perhaps both $\tau_1$ and $\tau_2$ can be estimated with reasonable accuracy provided the measurements are made at two suitably selected frequencies depending upon the type and nature of the molecule.

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