

DIELECTRIC ABSORPTION STUDIES IN CHLORO AND NITRO SUBSTITUTED ANILINES IN BENZENE*

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Dielectric absorption studies on four substituted anilines *viz.* 3-chloro aniline (A), 4-chloro-3-nitro aniline (B), 4-chloro-2-nitro aniline (C), 2-chloro-4-nitro aniline (D) have been made in the dilute solution of benzene and over a range of temperature in the microwave region of wave length 3.11 cm. The distribution parameter has been found to be low in the case of 3-chloro aniline, and for the other three molecules it is slightly high. The dielectric absorption was therefore, resolved by Higaši, Koga and Nakamura method which yielded two relaxation times $\tau_{(1)}$ and $\tau_{(2)}$. The $\tau_{(1)}$ and $\tau_{(2)}$ are widely different in the case of molecules B and C, showing the flexible nature of these molecules in the microwave field. The flexibility of the molecules increases as the relaxation time decreases. This is in agreement with our previous observations. The relaxation time has been found to be the highest in the case of 2-chloro-4-nitro aniline. The higher relaxation time is explained on the basis of hydrogen bonding taking place in case anilines in ortho position. These results are in agreement with the observations of Smyth et al.

Introduction

FISCHER [1] suggested that non rigidity was an important feature of anilines and predicted the rotation of $-\text{NH}_2$ group around C—N bond. Since then measurements have been made by many workers [2—7] to investigate the non rigidity of anilines. GRUBB and SMYTH [8] studied primary and secondary amines and diamines in viscous medium and in dilute solutions and have resolved the dielectric data in terms of two relaxation times. WILLIAM [9] has given a theoretical treatment and discussed that internal reorientation is feasible in amines. STOCKHAUSEN [10] and KLAGES [11] studied anilines and attributed the short group relaxation time to the inversion of non polar configuration of $-\text{NH}_2$ group through the plane of phenyl ring. FLORANTA and KADABA [6] studied the *o*-, *m*- and *para* chloro aniline both in pure liquid and in dilute solution and analyzed their results in terms of two relaxation times attributed to the rotation of molecule and the inversion of $-\text{NH}_2$ group. CHITOKU and HIGASI [12] studied anilines, methyl anilines, dimethyl anilines and *p*-nitro aniline and have reported very small values of distribution parameter for these compounds. According to the existing literature [1—12] amines behave as

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feebly flexible molecules, though not much work has been reported on trisubstituted anilines. Therefore, it was considered worthwhile to carry out dielectric measurements on *X*-band in the dilute solution of benzene and over the range of temperature (297–321 K) on 3-chloroaniline (A), 4-chloro-3-nitroaniline (B), 2-chloro-4-nitroaniline (C) and 4-chloro-2-nitroaniline (D). The effect of chloro and nitro group on the group relaxation process of $-\text{NH}_2$ group have been examined and the energy barriers associated with the different modes of relaxation have been evaluated. 3-chloroaniline has been used to compare and verify the results obtained by Higasi method and to study the systematic variation of chloro and nitro group in the *o*, *m*, and *para* position in the studied anilines.

Chemicals

The chemicals used were of purest quality available, obtained from B.D.H. England. The physical properties have been checked against the literature values. The solvent used in the measurements was benzene of the A.R. grade, obtained from B.D.H., England, and was distilled twice before use.

Experimental

The dielectric constant ϵ' and dielectric loss ϵ'' have been measured at *X*-band by the technique of ROBERTS and VON HIPPEL [13] latter modified by DAKIN and WORKS [14]. The static dielectric constant ϵ_0 was measured at 300 KHz by dipolemeter based on the principle of heterodyne beat method. The refractive indices of the different solutions were measured by Abbe's refractometer, the density and viscosity by pycnometer and Oswald's viscometer respectively. The measurements of ϵ' and ϵ'' are accurate up to $\pm 2\%$ and $\pm 5\%$ respectively.

The most probable relaxation time τ_{OH} and distribution parameter α have been evaluated by Higasi method [15], using equations (1) and (2)

$$\tau_{\text{OH}} = \frac{1}{\omega} \left[\frac{A^2 + B^2}{C^2} \right]^{\frac{1}{2(1-\alpha)}} \quad (1)$$

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

where

$$A = a''(a_0 - a_\infty)$$

$$B = (a_0 - a')(a' - a_\infty) - a''^2$$

$$C = (a' - a_\infty)^2 + a''^2$$

The slopes a_0 , a' , a'' and a_∞ are defined earlier [16] obtained by plotting weight fractions versus ϵ_0 , ϵ' , ϵ'' and ϵ_∞ and ω is the angular frequency selected for the measurements.

In the absence of multifrequency data being available Higasi, Koga and Nakamura method [17] has been utilized. It has been observed [18—20] in previous studies that $\tau_{(2)}$ stands for the molecular relaxation time τ_1 and the relaxation time $\tau_{(1)}$ associated with group process is a implicit function of τ_1 , τ_2 and C_2 defined by equation (3) and (4)

$$\tau_{(1)} = \frac{1}{\omega} \frac{a''}{(a' - a_\infty)}, \quad (3)$$

$$\tau_{(2)} = \frac{1}{\omega} \frac{(a_0 - a')}{a''}. \quad (4)$$

With no elaborate and accurate method being available for the measurement of a_∞ , the most general approximation $a_\infty = a_D$ has been applied to calculate the slope at infinite frequencies. The equations (3) and (4) are employed when the measurements of the slopes have been made very accurately. If $\tau_{(1)}$ and $\tau_{(2)}$ come out widely separated, it is a clear indication of more than a single relaxation process occurring in the system. Contrary to this, $\tau_{(1)} \approx \tau_{(2)}$ may be treated as a criterion [18] for the pure Debye type of dispersion and is indicative of a single relaxation time. The average relaxation time $\tau_{(0)} (= \sqrt{\tau_{(1)} \tau_{(2)}})$ is the square root of the product of $\tau_{(1)}$ and $\tau_{(2)}$.

The enthalpy of activation $\Delta H\tau_{(2)}$, $\Delta H\tau_{(0)}$ and $\Delta H\tau_{OH}$ have been determined from the straight line plots of $\log \tau_{(2)} \cdot T$, $\log \tau_{(0)} \cdot T$ and $\log \tau_{OH} \cdot T$ against $\frac{1}{T}$, wherever possible. The free energy of activation and the entropy of activation have been calculated by employing Eyring theory [21] of rate process.

Results

The value of the slopes a_0 , a' , a'' and a_∞ for all the four molecules in dilute solution of benzene and at varying temperatures have been reported in Table I. The most probable relaxation time together with the distribution parameter α are given in Table II. The value of dielectric relaxation time $\tau_{(1)}$, $\tau_{(2)}$ and $\tau_{(0)}$ and the enthalpies of activation $\Delta H\tau_{(2)}$ and $\Delta H\tau_{(0)}$ and $\Delta H\eta$ have been reported in Table III.

Discussion

(A) 3-Chloroaniline

The distribution parameter α for this molecule has been found to be sufficiently low (0.0—0.8) in the range of temperature 297—321 K. The most probable relaxation time at 297 K has been found to be 16.3 ps. This value agrees well with the relaxation time $\tau_0 (= 15.5 \text{ ps})$ by ELORANTA and KADABA [6] on *meta* chloro aniline using COLE—COLE [22] method. The small value of α indicates the rigid nature of molecule in the microwave field under investigation. In order to analyze, the dielectric dispersion data has been further analyzed by Higasi, Koga and Nakamura method [17], which yielded two relaxation time $\tau_{(1)} (= 14.2 \text{ ps})$ and $\tau_{(2)} (= 18.3 \text{ ps})$

Table I

Value of slopes a_0 , a' , a'' , a_∞ for the samples in benzene at different temperature

Compound	Temp. K	a_0	a'	a''	a_∞
(A) 3-chloro aniline	297	8.00	4.44	3.00	0.68
	305	7.00	4.20	2.95	0.49
	313	6.20	4.00	2.90	0.32
	321	5.06	3.25	2.20	0.27
(B) 4-chloro-3-nitro aniline	297	24.2	9.1	8.0	-1.25
	305	13.3	5.0	4.3	-0.66
	313	10.0	4.12	4.0	-0.40
	321	6.15	2.75	3.0	-0.30
(C) 4-chloro-2-nitro aniline	297	30.0	9.0	10.6	0.71
	305	25.0	7.4	9.1	0.48
	313	18.2	6.1	7.5	0.33
	321	13.8	6.0	5.71	0.31
(D) 2-chloro-4-nitro aniline	297	50.0	12.0	16.7	0.37
	305	40.1	10.5	14.3	0.38
	313	32.0	10.0	10.8	0.35
	321	26.2	9.5	9.5	0.32

at 297 K. The $\tau_{(1)}$ and $\tau_{(2)}$ values are quite close to each other, which indicates a single Debye type of dispersion occurring in the molecule. The results are in agreement with the observation of [6]. The smaller value group relaxation in the case of aniline was explained on the basis of high value of critical wavelength selected for the measurements. The dispersion in aniline occurs in the mm region and hence the absence of group relaxation time and distribution parameter in the higher wavelength region.

The equality in the values of $\tau_{(1)}$ and $\tau_{(2)}$ and very small value of distribution parameter α indicates that the dispersion is only feebly occurring in the 3.11 cm wavelength region.

The average relaxation time $\tau_{(0)}$ (=16.1 ps) agrees very well with τ_{OH} (=16.3 ps) at 297 K. These results are in agreement with our earlier studies on N-substituted amides [20], α -substituted benzyl cyanides [16] and the observation of HIGASI et al. on alkyl acetate [23].

Enthalpies associated with different processes involved in the dielectric absorption have been evaluated and found to be $\Delta H\tau_{OH}$ (=6.5 kJ mol⁻¹), $\Delta H\tau_{(2)}$ (=8.4 kJ mol⁻¹), $\Delta H\tau_{(0)}$ (=6.1 kJ mol⁻¹) and $\Delta H\tau_{(1)}$ (=10.5 kJ mol⁻¹). The enthalpy $\Delta H\tau_{(1)}$ is not very accurate due to the irregular variation of $\tau_{(1)}$. The enthalpy 6.5 kJ mol⁻¹ associated with most probable relaxation time τ_{OH} can be compared with the enthalpy of average relaxation time (=6.1 kJ mol⁻¹). The most probable enthalpies of activation are less than the corresponding free energies and so the entropies are usually negative. According to BRANIN and SMYTH [24] a negative entropy of activation indicates that there are fewer configurations possible in the activated state and for these configurations the activated state is more ordered than the normal state, which is in agreement with our previous studies [4, 5, 16]. The

enthalpy of viscous flow is highest because the process of viscous flow involves both rotation and translation, while the process of dipole orientation involves only the rotation of the molecules. Similar conclusion has been derived by HOLLAND and SMYTH [25].

(B) 4-Chloro-3-nitroaniline

The distribution parameter for this compound has been found to be (0.05—0.27) in the range of temperature 297—321 K. The most probable relaxation has been found to be $\tau_{OH} = 23.7$ ps at 297 K. This relaxation time can be compared with the relaxation time of 4-chloro aniline [6] (=21.5 ps) in benzene. The presence of $-\text{NO}_2$ group at the position 3 slightly increases the relaxation time of the molecule. Due to the high value of α the dielectric absorption was resolved, which gave two relaxation times $\tau_{(1)}$ (=12.7 ps) and $\tau_{(2)}$ (=31.1 ps). The $\tau_{(1)}$ and $\tau_{(2)}$ are widely different from each other, suggesting the flexibility of the molecule under the microwave field. The relaxation time $\tau_{(1)}$ associated with group process has been found to be irregular with temperature where as $\tau_{(2)}$, representing the molecular process is decreasing with the temperature. These observations are in agreement with the observation of SRIVASTAVA et al. [26] in N, N-dimethyl aniline and N, N-diethyl aniline.

The average relaxation time $\tau_{(0)}$ has been found to be 19.9 ps which is slightly less than τ_{OH} (=23.7 ps). This type of behaviour can not be ruled out because $\tau_{(0)}$ is the root average of $\tau_{(1)}$ and $\tau_{(2)}$. Such variations have been reported in the earlier work [16] of the author using Higasi, Koga and Nakamura method and also in the observations of HIGASI et al. [23].

Table II

Relaxation time evaluated using Higasi method and corresponding activation parameters

Compound	T K	α	τ_{OH}	ΔF_e kJ mol ⁻¹	ΔH_e kJ mol ⁻¹	ΔS_e J mol ⁻¹ deg ⁻¹
(A) 3-chloroaniline	297	.08	16.3	11.4	6.5	-16.5
	305	.01	14.1	11.4		-16.0
	313	—	12.8	11.5		-15.9
	321	.01	11.3	11.5		-15.6
(B) 4-chloro-3-nitroaniline	297	0.27	23.7	12.3	8.7	-12.1
	305	0.25	21.1	12.4		-12.1
	313	0.16	20.0	12.7		-12.7
	321	0.05	17.5	12.7		-12.5
(C) 4-chloro-2-nitroaniline	297	0.16	33.0	13.1	10.6	-8.4
	305	0.11	30.2	13.2		-8.5
	313	0.06	25.5	13.3		-8.6
	321	0.10	20.2	13.2		-8.1
(D) 2-chloro-4-nitroaniline	297	0.12	37.2	13.4	9.9	-11.8
	305	0.11	33.3	13.6		-12.1
	313	0.17	31.0	13.8		-12.5
	321	0.16	25.8	13.8		-12.5

The enthalpies associated with the various processes involved in the dielectric absorption have been found to be $\Delta H\tau_{OH}$ ($=8.7 \text{ kJ mol}^{-1}$), $\Delta H\tau_{(2)}$ ($=9.6 \text{ kJ mol}^{-1}$), $\Delta H\tau_{(0)}$ ($=4.9 \text{ kJ mol}^{-1}$); $\Delta H\eta$ ($=10.5 \text{ kJ mol}^{-1}$). The enthalpy for the average process $\Delta H\tau_{(0)}$ is not very accurate due to irregular variation of $\tau_{(0)}$, because $\tau_{(0)}$ is the square root of the product of $\tau_{(1)}$ and $\tau_{(2)}$ and $\tau_{(1)}$ is irregularly varying with the temperature. The enthalpy associated with most probable relaxation τ_{OH} for the molecule **B** ($=8.7 \text{ kJ mol}^{-1}$) has been found to be greater than **A**. This is in accordance with the bigger shape and size of the molecule **B** in comparison to molecule **A**.

The enthalpy, free energies and entropies are reported in Table II. The free energy ΔF_e ($=12.3\text{--}12.7 \text{ kJ mol}^{-1}$) and ΔS_e ($=12.1\text{--}12.5 \text{ J mol}^{-1} \text{ deg}^{-1}$) have been found in the range of temperature 297–321 K. The entropy found to be negative is similar to the molecule **A** and a slightly high value of free energy is due to high value of relaxation time in this molecule. These observations are in agreement with the earlier results of many workers [4, 5, 16, 24].

(C) 4-Chloro-2-nitroaniline

The distribution parameter α for this molecule has been found to be in the range of 0.06–0.16. The most probable relaxation time τ_{OH} for this molecule has been found to be 33.0 ps at 297 K. The relaxation time for this molecule has been found to be higher than that of **B** ($=23.7 \text{ ps}$), this can be attributed to the greater hindrance offered by $-\text{NO}_2$ group to the rotation of $-\text{NH}_2$ group in the position 2 than in the position 3.

The dielectric absorption has been further resolved which gave rise to two relaxation times $\tau_{(1)}$ ($=21.7 \text{ ps}$) and $\tau_{(2)}$ ($=34.6 \text{ ps}$). The average relaxation time for this molecule has been found to be 26.2 ps at 297 K.

The enthalpies involved in the various processes have been found to be $\Delta H\tau_{(2)}$ ($=14.7 \text{ kJ mol}^{-1}$), $\Delta H\tau_{(0)}$ ($=9.8 \text{ kJ mol}^{-1}$), $\Delta H\tau_{OH}$ ($=10.6 \text{ kJ mol}^{-1}$). The enthalpy associated with τ_{OH} for this molecule has been found to be greater than that of **A** and **B**. The enthalpy for the most probable relaxation process ($=10.6 \text{ kJ mol}^{-1}$) can be compared with the enthalpy of the average relaxation process ($=9.8 \text{ kJ mol}^{-1}$) within the experimental error, suggesting that the two processes are similar to one another.

The free energy ΔF_e ($13.1\text{--}13.3 \text{ kJ mol}^{-1}$) and a negative entropy ΔS_e ($=8.1\text{--}8.6 \text{ J mol}^{-1} \text{ deg}^{-1}$) have been found in the temperature range 297–321 K. The free energy has been found to be greater than **A** and **B** and the negative value of entropy is in agreement with the results obtained by previous workers [4, 5, 16, 24].

(D) 2-Chloro-4-nitroaniline

The distribution parameter α for this compound has been found to be in range of (0.11–0.17) in the range of temperature 297–321 K. The most probable relaxation time for this molecule has been found to be 37.2 ps which is sufficiently high in comparison to the other three molecules. Obviously this results from greater steric hindrance offered by $-\text{NH}_2$ group to the rotation of molecule by forming the intra-

molecular hydrogen bond between hydrogen atom of $-\text{NH}_2$ group and chlorine atom at position 2. The intramolecular hydrogen bonding is responsible for lowering the distribution parameter in comparison to the molecule **B** and **C** and increasing the overall relaxation time of the molecule. This is in agreement with the observations of SMYTH et al. [27] that the presence of $-\text{NO}_2$ group at the *para* position aids the delocalization of π -electrons between the nitrogen atom of $-\text{NH}_2$ group and the ring, which results in the intramolecular hydrogen bond, and consequently is responsible for long mean relaxation time and smaller distribution parameter for the *p*-nitro substituted aniline in benzene.

$\tau_{(2)}$ is very close to the most probable relaxation time τ_{OH} , showing that molecular process predominates in the system. Slight increase in α value with the temperature may be due to breaking of intramolecular hydrogen bond.

The enthalpies associated with different processes $\Delta H\tau_{(2)}$ and $\Delta H\tau_{\text{OH}}$ ($=9.9 \text{ kJ mol}^{-1}$), $\Delta H\tau_{(0)}$ ($=9.0 \text{ kJ mol}^{-1}$), $\Delta H\eta$ ($=10.5 \text{ kJ mol}^{-1}$) have been reported in Tables II., III. When compared to the enthalpies of molecule **A** and **B**. the

Table III

Relaxation times $\tau_{(1)}$, $\tau_{(2)}$ and $\tau_{(0)}$ and enthalpy of activation $\Delta H\tau_{(2)}$, $\Delta H\tau_{(0)}$, $\Delta H\eta$
Using Higasi, Koga and Nakamura method

Compound	T K	$\tau_{(1)}$ ps	$\tau_{(2)}$ ps	$\tau_{(0)}$ ps	$\Delta H\tau_{(2)}$ kJ mol ⁻¹	$\Delta H\tau_{(0)}$ kJ mol ⁻¹	$\Delta H\eta$ kJ mol ⁻¹
(A) 3-chloroaniline	297	14.2	18.3	16.1	8.4	6.1	10.5
	305	13.3	15.3	14.3			
	313	12.9	12.5	12.7			
	321	11.2	11.7	11.4			
(B) 4-chloro-3-nitroaniline	297	12.7	31.1	19.9	9.6	4.9	10.5
	305	12.7	28.8	18.8			
	313	14.6	24.2	18.8			
	321	16.2	18.7	16.2			
(C) 4-chloro-2-nitroaniline	297	21.7	34.6	26.2	14.7	9.8	10.5
	305	21.7	31.9	26.3			
	313	21.4	26.6	23.8			
	321	16.5	22.5	20.4			
(D) 2-chloro-4-nitroaniline	297	23.7	37.5	29.8	9.9	9.0	10.5
	305	23.2	34.1	28.1			
	313	18.5	33.6	24.9			
	321	17.1	29.0	22.3			

enthalpy of molecule **D** ($=9.9 \text{ kJ mol}^{-1}$) $>$ **B** ($=8.7 \text{ kJ mol}^{-1}$) $>$ **A** ($=6.5 \text{ kJ mol}^{-1}$). This may be due to the greater hindrance offered by $-\text{NO}_2$ group in *para* position. The more rigid nature of this molecule in comparison to **B** is perhaps responsible for the high value of enthalpy.

The free energy ΔF_a ($=13.4$ — 13.8 kJ mol^{-1}) and ΔS_a ($=11.8$ — $12.1 \text{ J mol}^{-1}\text{deg}^{-1}$) have been reported in Table II. The ΔS_a has been found to be negative, showing that fewer configurations are possible in the activated state and the activated state is more ordered than the normal state. These results are in agreement with our previous studies [4, 5, 16] and the study of BRANIN and SMYTH [24].

Conclusion

All the four investigated aniline molecules have been found to be flexible. The flexibility is small in the case of 3-chloroaniline (A), the rest three molecules 2-chloro-4-nitroaniline (D), 4-chloro-2-nitroaniline (C) and, 4-chloro-3-nitroaniline (B) have been found to be more flexible in microwave region under investigation. Although molecules B, C and D are of the same size and shape, still their behaviour in the microwave field, the relaxation time, distribution parameter, and dipolar relaxation parameters are found to be different. The relaxation times of the molecules are increasing as the flexibility is decreasing. These observations are consistent with our previous observations [4, 5].

Relaxation time of 4-Chloro-3-nitroaniline (=23.7 ps) is sufficiently small as compared to the compounds (C) and (D). This probably appears due to the vacant position 2 in this molecule. FONG et al. [28] have interpreted their results of larger relaxation times of 2,6-dimethyl aniline as compared to 2,5-dimethyl aniline in terms of greater steric hindrance offered to the rotation of $-\text{NH}_2$ group in the former molecule.

In the case of 2-Chloro-4-nitroaniline the relaxation time has been found to be the longest. This is attributed to the formation of hydrogen bond between the chlorine atom at position 2 and the hydrogen of $-\text{NH}_2$ group. These results are in agreement with the observation of SMYTH et al. [27].

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ИЗУЧЕНИЕ ДИЭЛЕКТРИЧЕСКОГО ПОГЛОЩЕНИЯ В ХЛОРО- И НИТРОЗАМЕЩЕННЫХ АНИЛИНАХ В БЕНЗОЛЕ

С. К. Саксена, Ц. Л. Гупта, М. Н. Шарма и М. Ц. Саксена

Проведено изучение диэлектрического поглощения четырех замещенных анилинов вицинального 3-хлоранилина (А), 4-хлоро-3-нитроанилина (В), 4-хлоро-2-нитроанилина (С), 2-хлоро-4-нитроанилина (Д) в разбавленных растворах в микроволновой области длин волн 3,11 см. Рассчитывали диэлектрическое поглощение по методу Хигаши, Кога и Накамура, по которому получены два релаксационных времени. Значения τ_1 и τ_2 значительно различались для молекул В и С, указывая на гибкость структуры этих молекул в микроволновом поле. Полученные результаты находятся в хорошем соответствии с данными, имеющимися в литературе.