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Study of Dielectric Relaxation Time and Thermodynamic Parameters in Some Polar Molecules in dilute solution of Benzene

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Abstract

Present communication reports the experimental values of the dielectric relaxation time (τ) of 4 Methoxyaniline, 4 Ethoxyaniline, 2 Nitroaniline, 2 Chloro, 4 Nitroaniline, 2,6 Dichloroaniline and 2 Methoxy, 3 Nitroaniline in dilute solution of benzene at wavelength 3.13 cm in the microwave region. The measurements have been made at 293, 303 and 313°K, in order to calculate the free energy of activation for dipole orientation process (ΔF_{τ}). The experimental values of τ have been correlated with the calculated value of τ obtained using different theories of dielectric relaxation time (τ). It is concluded from this comparative study that the Murty equation is a better representation of the dielectric relaxation phenomenon. Thermodynamical parameters like molar free energy of activation (ΔF_{τ}), molar enthalpy of activation (ΔH_{τ}) and molar entropy of activation (ΔS_{τ}) have been evaluated by considering the relaxation as the rate process. From the values of ΔF_{τ} for the various compounds investigated conclusion has been made that energy of activation increases with the size of molecule.

Key words: Dielectric relaxation time (τ), molar free energy of activation, molar enthalpy of activation and molar entropy of activation.

1. Introduction

The dielectric relaxation studies of organic polar complexes having different dipole bearing groups provide useful information about the structure of the molecules. Dielectric relaxation data obtained from the microwave absorption studies are expected to throw light on various types of molecular associations present in the solution. Dielectric relaxation studies of polar molecules in non-polar solvent from microwave absorption have been frequently attempted by number of research workers¹⁻³. It is very

much dependent upon the presence of different polar groups at various positions in the molecule and is sharply affected when one polar group is replaced by the other or the position of the group is changed with respect to other.

The investigation of dielectric relaxation phenomenon provides an important tool to explain the structural behavior of complex organic polar molecules in different non polar solvents. The well recognized approach to study the molecular interaction in the liquids makes use of physical properties like dielectric parameters. Investigation of the dielectric relaxation in a number of

organic compounds showed a wide disagreement between the observed values of the dielectric relaxation time (τ) and those calculated using the Debye equation⁴⁻⁶. The value of dielectric relaxation time (τ) calculated from Debye equation⁷ has been found 5 to 10 times of the experimental values. In order to remove these discrepancies Perrin⁹, Writz and their collaborators¹⁰ and Murty¹¹ gave different ideas to calculate τ .

Many workers¹²⁻¹⁵ have evaluated the dielectric relaxation time from Debye theory⁷ and found that the calculated values of τ range from 5 to 10 times the experimental values. The possibility of narrowing the gap between the experimental and calculated values stimulated the present work reported in this paper.

2. Experimental Details

All the compounds used were of pure quality obtained from M/S Central Drug House Ltd., New Delhi. The percentage purity of the investigated compounds ranged from 99.8 to 99.9%. The X-band microwave bench was used to measure wavelength in the dielectric medium and voltage standing wave ratio (VSWR) using a short circuiting plunger. The dielectric constant (ϵ') and dielectric loss (ϵ'') was calculated by the method of Heston *et al.*¹⁶. Dielectric relaxation time of molecular entities in benzene solution was calculated using single frequency concentration variation method of Gopala Krishna¹⁷. All the measurements were carried out at 293, 303 and 313 K by circulating water around the dielectric cell through a thermostat (Mittal Enterprise, New Delhi, India). Densities at different temperatures were measured by using a 10 ml specific gravity bottle and an electronic balance whose accuracy is 0.1 mg. The refractive index was measured using Abbe refractometer with sodium D light as source at different temperatures. The viscosities were determined with the help of Ostwald viscometer to an accuracy of $\pm 2\%$.

3. Theory :

The dielectric constant (ϵ') and dielectric loss (ϵ'') have been calculated by the method of Heston *et al.*¹⁶ using the following relations:

$$\epsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \quad (1)$$

And

$$\epsilon'' = \left(\frac{2\lambda_0^2}{\pi\lambda_d\lambda_g}\right)\left(\frac{d\rho}{dn}\right) \quad (2)$$

Where λ_0 , λ_c , λ_g , and λ_d are the free space wavelength, the

cut-off wavelength, the waveguide wavelength and the wavelength in the waveguide filled with solution, respectively. ρ is the inverse of voltage standing wave ratio (VSWR) and $(d\rho/dn)$ is the slope of ρ versus n curve, where $n = (1, 2, 3, \dots)$ such that $(n\lambda_d/2)$ represents the length of dielectric filled waveguide. The ϵ' and ϵ'' values from repeated measurements were reproducible within ± 0.05 and $\pm 1.67\%$, respectively.

The dielectric relaxation time (τ) has been calculated by using the Gopala Krishna's¹⁷ single frequency concentration variation method

$$X = \frac{\epsilon'^2 + \epsilon' + \epsilon''^2 - 2}{(\epsilon' + 2)^2 + \epsilon''^2} \quad (3)$$

$$Y = \frac{3\epsilon''}{(\epsilon' + 2)^2 + \epsilon''^2} \quad (4)$$

$$\tau = \frac{\lambda_0}{2\pi c} \left(\frac{dY}{dX}\right) \quad (5)$$

The energy parameters (ΔH_τ , ΔF_τ , and ΔS_τ) for dielectric relaxation process for compounds at different temperatures have been calculated by using Eyring *et al.*¹⁸, relations for the rate process. Following relations were used:

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta F_\tau}{RT}\right) \quad (6)$$

$$\Delta F_\tau = \Delta H_\tau - T\Delta S_\tau \quad (7)$$

Where ΔH_τ , ΔF_τ , and ΔS_τ are the enthalpy, free energy and entropy of activation, respectively for dielectric relaxation process and all other symbols have their usual meaning. ΔH_τ has been determined by slope of the plot of $\ln(T\tau)$ versus $1/T$, while ΔF_τ , and ΔS_τ are calculated using Eqs (6) and (7) respectively.

According to Debye's theory⁷ of the dielectric dispersion in polar liquids, the dielectric relaxation time is given by

$$\tau = \frac{4\pi\eta_1 a^3}{kT}$$

where symbols have their usual meanings.

Writz and Sperinol¹⁰ modified the Debye equation to the form given by

$$\tau = \frac{4\pi\eta_1 a_2^3}{kT} \left[6 \frac{a_1}{a_2} + \left(1 + \frac{a_1}{a_2}\right)^{-3} \right]^{-1} \quad (2)$$

Table 1. Values of Dielectric Relaxation Time (τ) (in 10^{-12} sec) at different temperatures for investigated compounds

Polar Compound	T ⁰ K	$\tau_{Exp.}$	τ_{Debye}	τ_{Writz}	τ_{Murty}
4 Methoxyaniline	293	3.86	68.97	12.23	3.92
	303	3.45	53.91	9.56	3.41
	313	3.13	52.18	9.25	3.05
4 Ethoxyaniline	293	11.05	76.75	14.07	11.28
	303	10.50	59.99	11.00	9.45
	313	9.98	58.07	10.64	8.53
2 Nitroaniline	293	9.37	61.75	10.57	9.10
	303	8.85	48.27	8.26	7.63
	313	8.03	46.27	7.92	6.88
2 Chloro,4 Nitroaniline	293	10.61	68.83	12.20	12.40
	303	9.75	53.80	9.53	10.40
	313	8.95	52.08	9.23	9.38
2,6 Dichloroaniline	293	12.49	75.72	14.21	10.81
	303	11.31	59.19	11.10	9.07
	313	10.58	57.29	10.75	8.18
2Methoxy, 3 Nitroaniline	293	13.26	77.08	14.14	12.18
	303	11.51	74.53	13.68	10.21
	313	10.30	72.15	13.24	9.22

Table 2. Thermodynamic parameters of investigated compounds at different temperatures

Name of the sample	Temperature K	ΔH_{τ} (kJ mol ⁻¹)	ΔF_{τ} (kJ mol ⁻¹)	ΔS_{τ} (kJ mol ⁻¹ K ⁻¹)
4 Methoxyaniline	293	5.47	7.70	-0.0076
	303		7.76	-0.0075
	313		7.85	-0.0076
4 Ethoxyaniline	293	1.36	10.26	-0.0304
	303		10.58	-0.0304
	313		10.87	-0.0303
2 Nitroaniline	293	1.96	9.86	-0.0270
	303		10.14	-0.0270
	313		10.30	-0.0266
2 Chloro,4 Nitroaniline	293	3.96	10.16	-0.0211
	303		10.38	-0.0211
	313		10.59	-0.0212
2,6 Dichloroaniline	293	3.82	10.56	-0.0230
	303		10.75	-0.0222
	313		11.02	-0.0230
2 Methoxy, 3 Nitroaniline	293	7.12	10.71	-0.0122
	303		10.80	-0.0121
	313		10.95	-0.0114

Where

$$a_i = \left[0.556 \left(\frac{M_i}{\pi d_i N} \right) \right]^{1/3} \quad (3)$$

Here, M_i , d_i and a_i are molecular weight, density, and radius of molecule, respectively.

Murty¹¹ has found a simple empirical equation for τ as

$$\tau = \frac{6\pi\eta_1\alpha}{(\epsilon_1 + 2)kT} \quad (4)$$

where α is the polarizability of the solute molecule and ϵ_1 is the dielectric constant of the solvent.

4. Results and Discussion

The experimental and calculated values of dielectric relaxation time (τ) of 4 Methoxyaniline, 4 Ethoxyaniline, 2 Nitroaniline, 2 Chloro, 4 Nitroaniline, 2,6 Dichloroaniline and 2 Methoxy, 3 Nitroaniline at 293, 303 and 313K are presented in Table 1. Table 2 represents the thermodynamic parameters of the investigated compounds at different temperatures.

4.1 Dielectric relaxation Time:

It is evident from Table 1 that the dielectric relaxation time of 2 methoxy 3 nitroaniline is the greatest among the six molecules. This is due to the steric hindrance produced by methoxy, nitro and amino group. The relaxation time of 4 ethoxyaniline is larger than that of 2 nitroaniline though both the molecules are of nearly same size. This can be explained due to the presence of rigid nitro group and strong steric hindrance between the nitro and amino groups at ortho position in later molecule. 2 chloro 4 nitroaniline exhibits a higher relaxation time than 2 nitroaniline which may be explained not only due to the larger molecular volume swept out for dipole orientation by it. The higher value 3,6 dichloroaniline as compared to that of 2 chloro 4 nitroaniline may be explained due to the greater steric hindrance between the two chloro groups in former molecule.

The experimental values of the dielectric relaxation time have been correlated with the calculated values obtained using the Debye equation, Writz equation and Murty equation. It is observed that when the equation of Writz and Sperinol is used, a better correlation is obtained. This is probably due to the introduction of a micro friction factor in the equation.

However, the values of τ calculated using Murty's equation are in close agreement with the experimental values. This is probably due to the polarizability of the molecules used to calculate the dielectric relaxation time (τ). This leads to the conclusion that the model of Murty is comparable in performance.

4.2 Thermodynamic parameters :

2 methoxy 3 nitroaniline molecules has the highest value for the free energy of activation for dipole relaxation and the 4 ethoxyaniline exhibits the lowest value. This can be attributed to the fact that the former molecule experiences maximum resistance in dipole rotation, whereas the latter experiences the least hindrance. It has been observed from Table 2 that activation energy for dipole orientation increases with size and shape of the molecules.

The free energy of activation (ΔF^\ddagger) for dielectric relaxation process is found to increase with increase in temperature. This may be due to the fact that with increase in temperature; the thermal agitation increases and dipole require more energy to be activated. The entropy of activation (ΔS^\ddagger) for dielectric relaxation process is found to be negative, suggesting that activated state is more ordered than the normal state. In activated state, the dipoles are more aligned than in normal state. Similar conclusions have been drawn by Narwade¹⁹ in case of some molecular mixtures.

5. Conclusions

It is concluded from this comparative study that the Murty equation is a better representation of the dielectric relaxation phenomenon. The activation energy for dipole orientation increases with size and shape of the molecules.

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