Ultra Scientist Vol. 28(2)B, 39-44 (2016).
www.ultrascientist.org

ISSN 2231-3478 (Print)
2319-8052 (Online)

Study of Dielectric Relaxation Time and Thermodynamic Parameters in Some Polar Molecules using Microwave Absorption Data

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(Acceptance Date 11th May, 2016)

Abstract

Present communication reports the experimental values of the dielectric relaxation time (τ) of five polar molecules of 2, 5-Dichloronitrobenzene, 3, 5- Dichloronitrobenzene, 2, 5-Dibromonitrobenzene, 4-Bromonitrobenzene and 2, 4 Dinitrochlorobenzene in dilute solution of benzene at wavelength 3.13 cm in the microwave region. The measurements have been made at 290, 300 and 310 ^{0}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. Thermo dynamical 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. The dielectric relaxation time is very intimately connected with the molecular motion and intramolecular interaction in molecular species[1-3]. 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 equation[4-6]. Debye[7] used the microscopic viscosity (η_1) of the solvent to calculate the relaxation time of polar molecules in dilute solutions which is determined by the interaction between the solvent molecules only while the relaxation time in case of a solution is entirely determined by the interaction between both the solvent and solute molecules. It was first successfully tackled by Hill[8], who suggested that the macroscopic viscosity of the solvent (η_1) should be replaced by the mutual viscosity of solute and solvent (η_{12}) which is a measure of solute- solvent interaction. The value of dielectric relaxation time (τ) calculated from Debye equation[7] has been found 5 to 10 times of the experimental values. In order to remove these discrepancies Perrin[9], Writz and their colabrators[10] and Murty[11] gave different ideas to calculate τ.

Many workers[12-15] have evaluated the dielectric relaxation time from Debye theory[7] 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 Krishna[17]. All the measurements were carried out at 290, 300 and 310 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 ± 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:

$$\varepsilon' = \left(\lambda_0 / \lambda_c\right)^2 + \left(\lambda_0 / \lambda_d\right)^2 \tag{1}$$

And

$$\varepsilon'' = \left(2\lambda_0^2 / \pi\lambda_d\lambda_g\right)\left(d\rho / dn\right) \tag{2}$$

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…….) 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 ±1.67, respectively.

The dielectric relaxation time (τ) has been calculated by using the Gopala Krishna's[17] single frequency concentration variation method

$$X = \frac{\varepsilon'^2 + \varepsilon' + \varepsilon''^2 - 2}{\left(\varepsilon' + 2\right)^2 + \varepsilon''^2} \tag{3}$$

$$Y = \frac{3\varepsilon''}{\left(\varepsilon' + 2\right)^2 + \varepsilon''^2} \tag{4}$$

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

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:

$$\tau = \frac{h}{kT}\exp\left(\Delta F\tau / RT\right) \tag{6}$$

$$\Delta F\tau = \Delta H\tau - T\Delta S\tau \tag{7}$$

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(Tτ) versus 1/T, while ΔF_τ, and ΔS_τ are calculated using Eqs (6) and (7) respectively.

According to Debye's theory[7] 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[19].

Writz and Sperinol[10] modified the Debye equation to the form given by

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

Where

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

Here, Mi, d_i and a_i are molecular weight, density, and radius of molecule, respectively. Murty[11] has found a simple empirical equation for τ as

$$\tau = \frac{6\pi\eta_1\alpha}{(\varepsilon_1 + 2)kT} \qquad (4)$$

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 2, 5-Dichloronitrobenzene, 3, 5- Dichloronitrobenzene, 2, 5-Dibromonitrobenzene, 4-Bromonitrobenzene and 2, 4 Dinitrochlorobenzene at 290,300 and 310K are presented in Table 1. Table 2 represents the thermodynamical parameters of the investigated compounds at different temperatures.

4.1 Dielectric relaxation Time :

It is observed from Table 1 that the dielectric relaxation time of 3,5 dichloronitrobenzene is greater than that of 2,5 dichloronitrobenzene, though both the molecules are of same size. This can be explained due to the fact that in 2,5 dichloronitrobenzene both chlorine atoms are at para position to each other hence the formed dipole is weak, while in 3,5 dichloronitrobenzene both chlorine atoms are at meta position to the nitro group which due to negative mesomeric effect produces greater steric hindrance to the rotation of the molecule resulting in higher value of relaxation time. 2, 5 dibromonitrobenzene has higher relaxation time than other compounds of the series which is due to the larger size of the molecule and strong polarity of the bromo group. 4 bromonitrobenzene exhibits the lowest relaxation time which can be explained not only due to the smallest size of the molecule but also due to the fact that the nitro and bromo groups are at para position with respect to each other. The dielectric relaxation time of 2,4 dinitrochlorobenzene is larger than that of 2,5 dichloronitrobenzene which is due to the larger size of the former molecule and the strong polarity of the nitro groups.

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 :

The free energy of activation for the process of dielectric relaxation increases with increasing temperature. This is due to the fact that at higher temperature the molecular collision rate increases with the result that energy required to bring molecules into activated state will also increase. Similar results have also been obtained by Raman Kumar[19] in case of some binary mixtures of tetrahydrofuran and N-methylacetamide. 2,5 dibromonitrobenzene molecule has the highest value for the free energy of activation for dipole relaxation and the 4 bromonitrobenzene exhibits

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

Polar Compound	T^0K	$\tau_{Exp.}$	τ_{Debye}	τ_{Writz}	τ_{Murty}
2,5 Dichloronitrobenzene	290	11.87	45.78	16.16	11.76
	300	10.65	50.79	17.93	9.96
	310	9.53	60.67	21.42	9.09
3,5 Dichloronitrobenzene	290	13.78	45.78	16.16	12.89
	300	12.45	50.79	15.23	11.93
	310	11.75	60.67	12.85	10.87
2,5 Dibromonitrobenzene	290	21.51	48.93	17.57	13.31
	300	19.56	54.27	19.49	11.27
	310	18.75	64.83	23.28	10.29
4 Bromonitrobenzene	290	8.21	42.99	14.93	11.18
	300	7.28	47.68	16.56	9.47
	310	6.17	56.96	19.79	8.64
2,4 Dinitrochlorobenzene	290	17.53	43.95	15.35	12.19
	300	14.28	48.76	15.57	10.33
	310	13.56	58.24	20.35	9.43

Table 2. Thermo dynamical 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 $mol^{-1}K^{-1}$)
2,5 Dichloronitrobenzene	290	9.41	10.36	-0.0033
	300		10.25	-0.0037
	310		10.14	-0.0042
3,5 Dichloronitrobenzene	290	9.57	10.82	-0.0043
	300		11.03	-0.0048
	310		11.24	-0.0053
2,5 Dibromonitrobenzene	290	9.32	11.78	-0.0084
	300		12.08	-0.0091
	310		12.41	-0.0099
4 Bromonitrobenzene	290	7.60	9.48	-0.0064
	300		9.65	-0.0067
	310		9.82	-0.0071
2,4 Dinitrochlorobenzene	290	8.27	10.99	-0.0104
	300		11.28	-0.0090
	310		11.57	-0.0107

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[19].

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.

References

1. S. Kumar, D. R. Sharma and N. Thakur, *Indian J. Pure Appl. Phys. 44,* 264 (2006).
2. P. Sivagurunathan, K. Dharmalingam, K. Ramachandran, B. Prabhakar Undre, P.W. Khirade, S.C. Mehrotra, *J. Mol. Liq. 133,* 139 (2007).
3. T. Kalaivini, S. Krishnan, *Indian J. Pure Appl. Phys. 47,* 880 (2009).
4. S.K. Vaish and N. K. Mehrotra, *Indian J. Pure Appl. Phys., 37,* 881(1999).
5. Ajay Kumar Singh, *Ultra Scientist, 23 (2)B,* 249 (2011).
6. A.K. Singh**,** *Physics and Chemistry of Liquids*, Vol. *54(4),* 523 (2012).
7. P. Debye, Polar Molecules, (Dover Publications, New York, 1945).
8. N.E. Hill, *Proc. Phys. Soc.*, 67,B, 695 (1954).
9. F. Perrin, *J. Phys. Radium, 5,* 497 (1934).
10. K. Writz and A. Sperinol, *Z. Naturforch. 8A,* 522 (1953).
11. C. R. K. Murty, *Indian J. Phys. 32,* 580 (1958).
12. A. Singh and N. K. Mehrotra, *J. Mol. Liq. 130,* 79 (2007).
13. A. Singh, A K Singh and N. K. Mehrotra, *J. Mol. Liq. 121,* 110 (2005).
14. A. Singh, A. K Singh and N. K. Mehrotra, *Bull. Chem. Soc. Jpn., 77,* 1 (2004).
15. A. K. Singh and N. K. Mehrotra, *Indian J. Phys., 79,* 1163(2005).
16. W. M. Heston (Jr.), A. D. Franklin, E. L. Hennelly and C. P. Smyth, *J. Am. Chem. Soc., 72,* 3443 (1950).
17. K. V. Gopala Krishna, *Trans. Faraday Soc., 53,* 767 (1957).
18. S. Glasstone, K. J. Laider and H. Eyring, The Theory of Rate Processes, (McGraw Hill, New York, 1941).
19. Raman Kumar, Vinod Sharma and V. S. Rangra, *Indian J Pure Appl. Phys., 48,* 415 (2010).