Pak. J. Chem. 3(2): 81-86, 2013
ISSN (Print): 2220-2625
ISSN (Online): 2222-307X
Full Paper
DOI: 10.15228/2013.v03.i02.p07

Effect of temperature on the dielectric relaxation time of binary mixture of 2-chloroaniline and 2-ethoxyethanol in 1,4-Dioxane solution using microwave absorption data

[1]B. G. Nemmaniwar, [2]S. S. Mokle and [1*]P. L. Kadam
[1*]Physics Research Laboratory, Department of Physics, Yeshwant Mahavidyalaya, Nanded – 431605 (MS) India.
[2]Department of Chemistry, Yeshwant Mahavidyalaya, Nanded – 431605(MS) India.
E-mail: *pothajikadam@yahoo.com, bhupesh.nemmaniwar@rediffmail.com

ABSTRACT
The dielectric constant (ε′),dielectric loss (ε′′), relaxation times (τ) and the dipole moments (μ) of the binary mixtures of different molar concentrations of 2-chloroaniline C_6H_6ClN in the binary mixtures of 2-chloroaniline (2-CA) and 2-ethoxyethanol (2-EE) $C_4H_{10}O_2$ in 1,4-dioxane $C_4H_{10}O_2$ solutions were calculated by using standard standing wave microwave X- band techniques and Gopala Krishna's single frequency 10.985 GHz concentration variational method at different temperatures 20,30,40,50^{0}C. The dielectric relaxation process was found to be an activated process. The dielectric relaxation process of binary mixtures containing 30% mole-fraction of 2-CA were calculated at the respective given temperatures. On the basis of the observations, it was found that the dielectric relaxation process could be treated as the rate process like the viscous flow process. The dipole moment of pure and binary mixtures were calculated with varying temperatures. The solute-solute and solute-solvent molecular associations were predicted. Dipole moment (μ) of 2-CA and 2-EE non- linearly increased with rise in temperature.

Keywords: Dielectric relaxation, Binary mixtures, 2-chloroaniline and 2-ethoxyethanol, Dipole moment and Microwave absorption studies.

1. INTRODUCTION
2-Chloroaniline is solute having dielectric constant ε′= 13.4 at 20^{0}C and dipole moment μ =1.78D at 20^{0}C [1].Its melting point is -1.94^{0}C and boiling point 208.8^{0}C [2]. 2-chloroaniline is used as an intermediate in the production of a number of products, including agricultural chemicals, azo- dyes, pigments and pharmaceuticals. It is also used in petroleum solvents. The second constituent of the binary mixture is 2-ethoxyethanol (2-EE) is an important solvent having dielectric constant ε′ = 29.6 at 24^{0}C and dipole moment μ =2.24D at 30^{0}C [1]. Its melting point is -90^{0}C and boiling point is 135^{0}C [3]. 2-Ethoxyethanol is used in varnish removers, degreasing solutions, used in printing industries and an additive for jet fuel to prevent ice build-up. Dielectric relaxation studies of polar molecular in non-polar solvents using microwave absorption techniques have been studied by many researchers [4-11]. From solvent point of view, it is possible to have binary mixtures of 2-CA and 2-EE having dielectric constant and dipole moment value in between that of 2-CA and 2-EE. Hence, the dielectric relaxation process in the binary mixture of 2-CA and 2-EE has been studied to understand the molecular association in the whole concentration range of (2-CA) in the binary mixture. Dielectric relaxation of liquid mixtures in the microwave region has been investigated to Characterize different types of molecular interactions such as self-association, solute-solute and solute-solvent type of the molecular association among the polar molecules in the solution[12-14]. This is because of the capacity of microwaves to detect the weaker molecular interactions. The dielectric measurements have been made for the binary mixtures of different mole fractions of 2-CA (0.0, 0. 23457, 0.47899, 0.73391, 1.0) at different temperatures 20^0, 30^0, 40^0 and 50^0 C. The dielectric relaxation process has been found to be an activated process. From the experimental observations it is found that the dielectric relaxation process is a rate process like that of the viscous flow process. Solute-solute and solute-solvent types of the molecular associations for 2-CA have been proposed.

2. EXPERIMENTAL METHOD

2.1 *Materials*
2-Chloroaniline (GC Grade) was obtained from Merck-Schuchardt, Germany.2-Ethoxyethanol and 1,4-dioxane (AR Grade) were purchased from M/S Sd. Fine chemical, Mumbai, India without further purification the two (2-CA+2-EE) liquids according to their proportions by volume were mixed well and kept 6 hours in well stoppered bottles to ensure good thermal equilibrium. These liquids used as solute and solvent.

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 set up was tuned at microwave frequency 10.985 GHz. The experimental techniques of Heston *et.al.* used by Nemmaniwar *et al* [15] for microwave measurements. All the measurements were carried out at temperatures 20^0, 30^0, 40^0 and 50^{0}C by circulating ethylene glycol+water around the dielectric cell and temperature was thermostically controlled with $\pm$ 0.5^{0}C. Using Nevitech pvt. Ltd. Mumbai

*Corresponding Author
Received 21st March 2013, Accepted 15th May 2013

India. The whole of the equipment was standardized with the help of standard materials like methanol and ethylene glycol+water (40:60). Microwave power measured by PM-437 (Attest) power meter, Chennai, India using source of Reflex klystron 2 K 25 (USSR). The densities and viscosities of the pure components and their binary mixtures were measured by using DMA 35 portable vibrating density meter. Anton paar Autria (Europe) was having accuracy of density 0.001 gm/cm^3, repeatability 0.0005 gm/cm^3 and resolution 0.0001 gm/cm^3 [16] and viscosity by LV DV II-pro Brook ield viscometer with an accuracy of $\pm$1% [17] (USA).Rectangular wave guide working TE_{10} mode, 10 dB, Vidyut Yantra Udyog, India. To hold the liquid sample in the liquid cell, thin mica window whose VSWR and attenuation were neglected is introduced between the cell and rest of microwave bench.

3. RESULTS AND DISCUSSION

The dielectric constant (ε′), dielectric loss (ε′′), relaxation time (τ) and dipole moment (μ) for the binary mixture of 2-CA+2-EE in 1,4-dioxane solution at 20^0, 30^0, 40^0 and 50^0C for different mole fraction containing 0, 30,50,70 and 100 mol% of 2-CA+2-EE in 1,4-dioxane solution. The microwave techniques have been used calculated by the method suggested by Heston *et al* [15] .Equations 1 and 2 have been used.

$$\varepsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \qquad \text{……… (1)}$$

$$\varepsilon'' = \frac{2}{\pi}\left(\frac{\lambda_0}{\lambda_d}\right)^2 \cdot \frac{\lambda_g}{\lambda_d}\left(\frac{d\rho}{dn}\right) \qquad \text{……… (2)}$$

Where $\lambda_0, \lambda_c, \lambda_g$ and λ_d are the free space wavelengths, the cut-off wavelength, the waveguide wavelength and the wavelength in the waveguide filled with solution in centimeter respectively. ρ is inverse of voltage standing wave ratio (VSWR) and $d\rho / dn$ is the slope of ρ versus n, where n=1,2,3…… such that $(n\lambda_d / 2)$ represents the length of the dielectric filled waveguide. The ε′and ε′′ values were estimated to be reproducible within $\pm 0.5\%$ and $\pm 1\%$ respectively. The relaxation times (τ) and the dipole moment (μ) have been calculated by using equation 3-6 by the single frequency concentration variational method of Gopala Krishna[18].

$$X = \frac{\varepsilon'^2 + \varepsilon''^2 - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} \qquad \text{……… (3)}$$

$$Y = \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} \qquad \text{……… (4)}$$

$$\mu^2 = \frac{9kTM}{4\pi N d_0}\left[1 + \left(\frac{dY}{dX}\right)^2\right]\frac{dX}{dW} \qquad \text{……… (5)}$$

$$\tau = \frac{\lambda_0}{2\pi c}\left(\frac{dY}{dX}\right) \qquad \text{……… (6)}$$

Where N is the Avogadro number, M is the molecular weight of polar substance in gm/mol, W is the weight fraction and d_0 is the density of solution in gm/cm³. The values of ε′ and ε′′ for the binary mixture 2-CA+2-EE in the 1,4-dioxane solution have been calculated using the short-circuited waveguide method of Heston *et.al.*[15]. This method is highly accurate for the measurement of ε′ and ε′′ of polar mixtures in dilute solutions of non-polar solvent at very low concentrations. The accuracy in measurements ε′ and ε′′ values was $\pm$1% and $\pm$2% respectively. From observations Table 1-4, the variation of ε′ and ε′′ with weight fraction of solute in 1,4-dioxane for all binary mixtures is found to be linear. This shows that there is no change in the nature of the rotating molecular entities in the 1, 4-dioxane solution. This ensures the applicability of the Debye theory[19] and that of Gopala Krishna’s method in the studied concentration range of the binary mixtures in the 1,4-dioxane solutions. The relaxation times depend upon the size and shape of the rotating molecular entities in the solution. This method determines the average value of the relaxation time for the participating molecular entities in the solution. The linear variation of the relaxation time from its value corresponding to one constituent to the value corresponding to the other constituent with the mole-fraction variation in the whole concentration range may be taken as the absence of any solute-solute association in the mixtures. On the other hand, non-linear variation of the relaxation time with the mole-fraction is interpreted as the possible solute-solute molecular association in the binary mixtures. So if the relaxation time of 2-CA+2-EE binary mixture increases linearly with the mole fraction of 2-CA ($X_{2\text{-}CA}$), no molecular association can be inferred. However, if the relaxation time 2-CA+2-EE binary mixture increase non-linearly, a solute-solute type of molecular association between 2-CA and 2-EE may be inferred. The variation of τ versus $X_{2\text{-}CA}$ at different temperatures is shown in Fig-1.

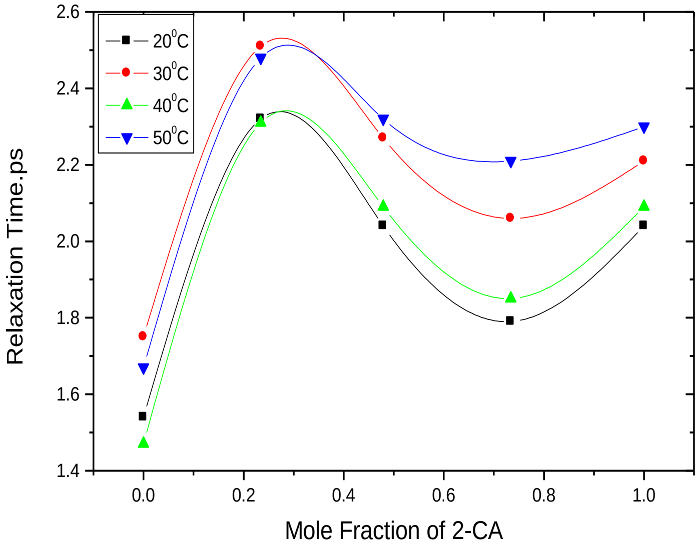

Fig- 1: Relaxation time (τ) versus mole fraction of 2-CA in 2-CA+2-EE binary mixture in 1,4-dioxane solution at different temperatures.

The relaxation time of 2-CA+2-EE binary mixture increase as the mole fraction of 2-CA in 2-CA+2-EE increase from X= 0 to X= 0.3. After this mole fraction, relaxation start decreases and finally drops to a pure 2-CA mole fraction of 2-CA equal to 1.00 at all temperatures. The plots of τ versus $X_{2\text{-}CA}$ show a maximum relaxation time at $X_{2\text{-}CA}$=0.23457.This solute-solute type of molecular association is maximum for 30 mol% of 2-CA in 2-CA+2-EE binary mixture. For this concentration, the relaxation time of the molecular entities becomes longer than that of the individual molecules. The molecular association between 2-CA and 2-EE is maximum at a 30:70 mol% ratio and then decrease at higher mol% of 2-CA in binary mixtures. In its whole concentration range, the relaxation time of 2-CA+2-EE binary mixture remains longer that of pure 2-CA. Therefore, the solute-solute type molecular association between 2-CA and 2-EE is indicated in its entire concentration range. In view of above results, it is proposed that in the binary mixtures of 2-CA and 2-EE, 2-CA exists in the dimer structure resulting because of H-bonding and dimer structure of 2-CA interact with the 2-EE molecules so as to give the maximum values of relaxation time at 30 mol% 2-CA binary mixture. This type of molecular associations has been proposed in Fig 2 The value of dipole moment of 2-CA binary mixture with 100% mole fraction of 2-CA in the binary mixture depends on the temperature. Table 1-4. This indicates the presences of solute-solvent molecular association of pure 2-CA in 1, 4-dioxane solution. The value of dipole moment of 2-EE binary mixture with 0.00 mole fraction of 2-CA in binary mixture Table 1-4 is found to be slightly change with temperature. This could be explained on the basis of the solvent effects [20]. The change in dipole moment with temperature may be due to the stretching of bond moment and to the change in bond angle. The dipole moment value of 2-CA slightly non-linearly increases with the rise in temperature in 1, 4-dioxane solution.

This predicts the solute-solvent type of molecular association for 2-CA in the 1,4-dioxane solution. Solute-solute association can be interpreted because of the molecule association arising due to hydrogen bonding between 2-ethoxyethanol and 2-chloroaniline. In this hydrogen bonding δ^+ on hydrogen of hydroxyl group of 2-ethoxyethanol that form hydrogen bonding with nitrogen of 2-chloroaniline as shown in Fig 2. It may be explain on the basis that the dielectric relaxation process involves the rotation of molecular entities whereas in the viscous flow process.

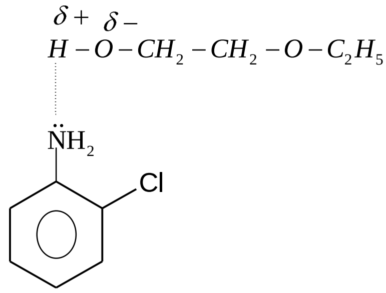

Fig-2: Solute-solute molecular association between 2-CA and 2-EE

Solute- solvent association can be interpreted because of the molecule association arising due fractional positive charge on hydrogen of 2-ethoxyethanol and lone pair electron present on oxygen of 1,4-dioxane is shown in Fig.3.

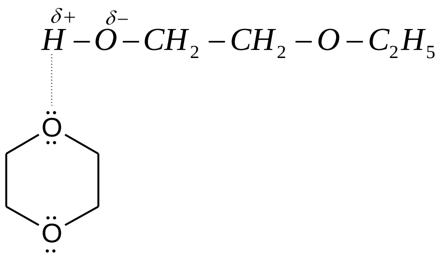

Fig-3: Solute-solvent molecular association of 2-EE in 1,4-dioxane solution

Table-1: Dielectric constant (ε′), dielectric loss (ε″), relaxation time (τ) and dipole moment (μ) of different mole fraction of 2-CA in (2-CA+2-EE) binary mixture in 1, 4-dioxane at 20^0C temperature.

Mole Fraction	Weight Fraction (W)	ε′ (±0.5%)	ε″ (± 1%)	τ (P.Sec)	μ(D) Debye
0	0.052875	2.14540	0.0980	1.54	1.42
	0.100439	2.3758	0.1281		
	0.143455	2.5049	0.1507		
	0.1872544	2.5056	0.1580		
0.23457	0.057037	2.0480	0.0961	2.32	1.38
	0.107919	2.2408	0.1316		
	0.153591	2.3385	0.1553		
	0.194814	2.3591	0.1659		
0.47899	0.060955	1.8811	0.0726	2.04	1.63
	0.114906	2.1846	0.1198		
	0.162994	2.2214	0.1363		
	0.206127	2.2982	0.1548		
0.73391	0.064481	1.9892	0.08642	1.79	1.70
	0.121150	2.2982	0.1292		
	0.171346	2.3591	0.1556		
	0.216117	2.4896	0.1799		
1	0.067923	1.8811	0.0726	2.04	1.58
	0.127205	2.1846	0.1198		
	0.179398	2.2214	0.1363		
	0.225700	2.2982	0.1548		

Table-2: Dielectric constant (ε′), dielectric loss (ε″), relaxation time (τ) and dipole moment (μ) of different mole fraction of 2-CA in (2-CA+2-EE) binary mixture in 1, 4-dioxane at 30^0C temperature.

Mole Fraction	Weight Fraction (W)	ε′ (±0.5%)	ε″ (± 1%)	τ (P.Sec)	μ(D) Debye
0	0.052875	2.0974	0.01054	1.75	1.54
	0.100439	2.3352	0.1342		
	0.143455	2.4704	0.1556		
	0.1872544	2.4864	0.1610		
0.23457	0.057037	2.0691	0.0893	2.51	1.75
	0.107919	2.3500	0.1278		
	0.153591	2.3891	0.1503		
	0.194814	2.5597	0.1627		
0.47899	0.060955	2.1454	0.0980	2.27	1.49
	0.114906	2.3758	0.1281		
	0.162994	2.5049	0.1507		
	0.206127	2.5056	0.1580		
0.73391	0.064481	2.3385	0.1270	2.06	1.70
	0.121150	2.6168	0.1679		
	0.171346	2.7692	0.2016		
	0.216117	2.8878	0.2235		
1	0.067923	2.008	0.0886	2.21	1.48
	0.127205	2.1846	0.1200		
	0.179398	2.2982	0.1482		
	0.225700	2.3591	0.1632		

Table-3: Dielectric constant (ε′),dielectric loss (ε″), relaxation time (τ) and dipole moment (μ) of different mole fraction of 2-CA in (2-CA+2-EE) binary mixture in 1, 4-dioxane at 40^{0}C temperature.

Mole Fraction	Weight Fraction (W)	ε′ (±0.5%)	ε″ (± 1%)	τ (P.Sec)	μ(D) Debye
0	0.052875 0.100439 0.143455 0.1872544	2.2105 2.4647 2.5240 2.6049	0.0944 0.1260 0.1415 0.1572	1.47	1.53
0.23457	0.057037 0.107919 0.153591 0.194814	2.0280 2.2400 2.3182 2.3591	0.0893 0.1278 0.1503 0.1627	2.31	1.50
0.47899	0.060955 0.114906 0.162994 0.206127	1.1989 2.2214 2.2982 2.3591	0.0855 0.1160 0.1485 0.1613	2.09	1.59
0.73391	0.064481 0.121150 0.171346 0.216117	2.0480 2.4228 2.4440 2.5839	0.0767 0.1270 0.1492 0.1768	1.85	1.82
1	0.067923 0.127205 0.179398 0.225700	1.9890 2.2214 2.2982 2.3591	0.0855 0.1160 0.1485 0.1613	2.09	1.53

Table-4: Dielectric constant (ε′), dielectric loss (ε″), relaxation time (τ) and dipole moment (μ) of different mole fraction of 2-CA in (2-CA+2-EE) binary mixture in 1, 4-dioxane at 50^{0}C temperature.

Mole Fraction	Weight Fraction (W)	ε′ (±0.5%)	ε″ (± 1%)	τ (P.Sec)	μ(D) Debye
0	0.052875 0.100439 0.143455 0.1872544	2.0691 2.3500 2.3891 2.5597	0.0956 0.1406 0.1547 0.1844	1.67	1.77
0.23457	0.057037 0.107919 0.153591 0.194814	2.0807 2.1756 2.4228 2.4896	0.0951 0.1429 0.1882 0.1935	2.48	1.66
0.47899	0.060955 0.114906 0.162994 0.206127	2.0480 2.2401 2.3385 2.3591	0.0961 0.1316 0.1553 0.1659	2.32	1.47
0.73391	0.064481 0.121150 0.171346 0.216117	2.4070 2.4655 2.5759 2.7921	0.0999 0.1184 0.1348 0.1688	2.21	1.35
1	0.067923 0.127205 0.179398 0.225700	2.1136 2.4670 2.6334 2.6845	0.0685 0.1226 0.1582 0.1774	2.30	1.83

4. CONCLUSIONS

The dielectric relaxation parameter for 2-CA and 2-EE in 1, 4-dioxane was determined using standard microwave standing wave techniques and single frequency concentration variation method of Gopala Krishna. The non-linear variation of the relaxation time with the change in mole-fraction of 2-CA in the binary mixture predicted the presence of solute-solute and solute-solvent molecular association the relaxation time attained a maximum value at 30 mol% of 2-CA in the binary mixture. The value of the dipole moment of 2-CA+2-EE was to be found slightly non-linearly increased with the rise in temperature.

5. ACKNOWLEDGEMENT
The authors are thankful to the Principal, Yeshwant Mahavidyalaya Nanded for providing necessary laboratory facilities.

6. REFERENCES
1. Dean's *hand book of organic chemistry*, George. W. Gokel, *Digest of literature on dielectric's* **(1971)**, 35**.** National Academy of science Washington.D.C **(1973)**.
2. *Hand book of Physical and chemical Properties and environmental fate for organic chemicals*. Second edition. Vol. IV., Donald Mackay, Wan Ying Shiu, Kuo-ching Ma, Sum Chi Lee, **(2006)**, CRC Press, Taylor and Francis Group. Chapter 16.
3. *Sitting's hand book toxic and hazardous chemicals and carcinogens*. By Richard. P. Pohanish. V^{th} Edition. **(2008)** Published by William-Aandrew-INC. Norwich, N.Y.13815.
4. Thenappan, T., and Sankar, U., *Indian J Pure & Appl Phys*. **(2004)**, 42, 435.
5. Rangara, V. S., and Shrama, D. R., *Indian J Pure & Appl Phys*. **(2003)**, 41,630.
6. Nages, T., and Sharma, D. R., *Indian J Pure & Appl Phys.* **(2000)**, 38,328.
7. Abd, S. L., Messieh, E. I., *J. Mol. Liq*. **(2002)**, 95,167, http://dx.doi.org/10.1016/S0167-7322(01)00278-1.
8. Sharma, A. K., Sharma, D. R., Sharma, K. C., and Gill, D. S., *Zeitschrift fur Physikaliche Chemie Nue Folge, Bd.* **(1984)**, 141, 15.
9. Sit, S. K., Ghosh, N., Saha, N., and Acharya, S., *Indian J Phys*. **(1997)**, 71B, 553.
10. Vyas, A. D., and Rana, V. A., *Indian J Pure & Appl Phys*. **(2002)**, 40, 69.
11. Sharma, A., and Sharma, D. R., *Indian J Pure & Appl Phys*. **(1992)**, 30, 185.
12. Krishnamurthy, S. S., and Sundrarajan, S., *J. Phys Chem*. **(1969)**, 73, 4036, http://dx.doi.org/10.1021/j100846a002.
13. Higasi, K., *Bull Chem Soc Japan.* **(1966)**, 39, 2157, http://dx.doi.org/10.1246/bcsj.39.2157.
14. Dhull, J. S., Sharma, D. R., Gill, D. S., and Lakshminarayana, K. N., *Indian J Phys*. **(1982)**, 56B, 334.
15. Heston, W. H., Franklin (Jr), A. D., Hennely, E. L., and Smyth, C. P., *J. Am. Chem Soc*. **(1950)**, 72, 3443, http://dx.doi.org/10.1021/ja01164a033.
16. Vural, U. S., Muradoglu, V., and Vural, S., *Bull. Chem. Soc. Ethiop***. (2011)**, 25, 111.
17. Maharolkar, A.P., Sudke, Y., Kamble, S., Tidar,A., Murugkar,A.G., Patil,S. S., Khirade,P. W. and Mehrotra,S. C., *Inter.J. of Chem*.**(2010)** 2, 250.
18. Gopala Krishna, K. V., *Trans Faraday Soc*. **(1957)**, 33, 767, http://dx.doi.org/10.1039/tf9575300767.
19. Debye, P., *Polar molecular*, The chemical Catalog Company, Inc., New York. **(1929)**, 679.
20. Hill, N. E., Vaughan, W. E., Price, A. H., and Mansel, D., *Dielectric Properties and molecular behavior*, Vol. 3, Van nostrand Reinhold Company, London. **(1969)**, Chap. 4.