INTERNATIONAL JOURNAL FOR INNOVATIVE RESEARCH IN MULTIDISCIPLINARY FIELD
ISSN: 2455-0620 [Impact Factor: 6.719]
Monthly, Peer-Reviewed, Refereed, Indexed Journal with IC Value : 86.87
Volume - 8, Issue - 8, August - 2022 Publication Date: 31/08/2022

DOIs:10.2015/IJIRMF/202208013 --:-- Research Paper

Dielectric Relaxation and Thermodynamic Parameters of Iso-Amyl Alcohol, Ethylenediamine and their Binary Mixtures in 1,4 - Dioxan

B. S. Narwade
Dept. of Physics, Degloor College, Degloor Dist: Nanded Maharashtra (India)
Email: narwadebs123@gmail.com

Abstract: *The values of dielectric constant ($\in'$) and loss factor ($\in''$) have been experimentally determined for Iso- amyl alcohol, ethylenediamine and their binary mixture in 1-4, dioxan at different temperatures 9.85 GHz microwave frequency. The values of $\in'$ and $\in''$ have been used to evaluate the relaxation time (τ) and dipole moment (μ) by employing Gopala Krishna's method. Thermodynamic parameters also have been calculated for dielectric relaxation as well as for viscous flow process. The nonlinear behavior of relaxation time with mole fraction reveals presence of solute-solute molecular association in the mixture*

Key Words: *Relaxation time, Dipole moment, Dielectric relaxation, Thermodynamic parameters.*

1. INTRODUCTION:

Dielectric relaxation in the mixture of polar liquids in non-polar solvent has evoked considerable interest. Since in these systems apart from self-association, there is possibility of hetro-association. The dielectric relaxation depends upon the molecular size, shape, intra and intermolecular interaction. Therefore, study of dielectric relaxation can be used for knowledge of internal rotation, complex formation, solute-solute and solute-solvent molecular association in the mixture. Several workers [1-6] have done extensive work on dielectric behaviour of polar liquids and their binary mixtures in non-polar solvent.In the present chapter the dielectric relaxation study of Iso-amyl alcohol (*IAA),* ethylenediamine (*EDA*) and their binary mixtures in 1,4-dioxan is carried out for different mole fraction of *EDA* at different temperature. The study is expected to provide better understanding of the nature of molecular association in the mixture.

2. LITERATURE REVIEW:

Dielectric relaxation studies of polar molecules in non-polar solvent from microwave absorption have been frequently attempted by a number of research workers [1-6]. Rajesh Kumar [1] et al., have calculated the relaxation time (τ), dipole moment (μ) and energy parameters of binary mixtures of N-methyl formamide (*NMF*) and dimethylsuphoxide (*DMSO*) in benzene and predicted solute-solute type of molecular association in the mixture. Rana and Vyas [2] have evaluated relaxation time (τ) and distributed parameters for 3-bromo aniline and its mixtures with 1-propanol in dilute solution of benzene. They found more than one relaxation processes in the system and interaction between constituent moleculesIn the present chapter the dielectric relaxation study of Iso-amyl alcohol (*IAA),* ethylenediamine (*EDA*) and their binary mixtures in 1,4-dioxan is carried out for different mole fraction of *EDA* at different temperature. The study is expected to provide better understanding of the nature of molecular association in the mixture.

3. MATERIAL:

Iso-amyl alcohol (*IAA*) and ethylenediamine (*EDA*) A.R. Grade supplied by M/s S.D. Fine Chemicals were used without further purification. 1,4-dioxane AR grade supplied by M/s E-Merk India Ltd., also used without further purification. The liquids were mixed according to their proportions by volume and kept for six hours to ensure good thermal equilibrium.

4. EXPERIMENTAL METHOD:

The X-band microwave bench was used to measure wavelength in dielectric (λ_d) and voltage standing wave ratio (*VSWR*) using short circuit plunger. To hold the liquid sample in the cell, a thin mica window whose *VSWR* and attenuation were neglected, is introduced between the cell and rest of microwave bench. is switched on. The dielectric

constant ($\in'$) and dielectric loss ($\in''$) of *IAA*, *EDA* and their binary mixtures at different temperature were calculated by using following equations[12]

$$\in' = \left(\frac{\lambda_o}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \qquad [1]$$

$$\in'' = \left(\frac{2}{\pi}\right)\left(\frac{\lambda_o}{\lambda_d}\right)^2\left(\frac{\lambda_g}{\lambda_d}\right)\left(d\rho/dn\right) \qquad [2]$$

where λ_o, λ_c, λ_g and λ_d are the free space wavelength, the cutoff wavelength, guide wavelength and wavelength in dielectric respectively. ρ is the inverse voltage standing wave ratio (*VSWR*) and $d\rho/dn$ is the slope of ρ versus *n* where *n* = 1,2,3------ such that $n\frac{\lambda_d}{2}$ represents the length of dielectric filled in wave guide. The values of λ_d, $d\rho/dn$ for different weight fraction of solute in 1,4-dioxan. The calculated values of ($\in'$) and ($\in''$) for different concentration and at different temperatures have been utilized in evaluating the relaxation time (τ) and dipole moment (μ) following Gopal Krishna's [7] method.

$$x = \frac{\in'^2 + \in' + \in''^2 - 2}{(\in'+2)^2 + \in''^2} \qquad [3]$$

$$y = \frac{3\in'}{(\in'+2)^2 + \in''^2} \qquad [4]$$

$$\tau = \frac{\lambda_o}{2\pi c} \times \frac{dy}{dx} \qquad [5]$$

$$\mu = \left[\frac{9KTM}{4\pi Nd} \times \left\{1 + \left(\frac{dy}{dx}\right)^2 \frac{dx}{dw}\right\}\right]^{1/2} \qquad [6]$$

where *c* is the velocity of electromagnetic waves, *k* is the Boltzman's constant, *N* is Avogadro's number, *M* is molecular weight of solute, *d* is the density of the solvent, *T* is absolute temperature, and *w* is the weight fraction of solute. The slope of the line drawn between *x* and *y* used for determining the value of relaxation time (τ) and the slope of line *x* and *w* used for calculating the dipole moment (μ).

The energy parameters, free energy (ΔF_τ), enthalpy (ΔH_τ) and the entropy of activation (ΔS_τ) for the dielectric relaxation process and the corresponding parameters for the viscous flow (ΔF_η), (ΔH_η) and (ΔS_η) have been calculated using the Eyrings equations [13].

$$\tau = \left(\frac{h}{KT}\right) \times \exp\left(\frac{\Delta F_t}{RT}\right) \qquad [7]$$

$$\Delta F_\tau = \Delta H_\tau - T\Delta S_\tau \qquad [8]$$

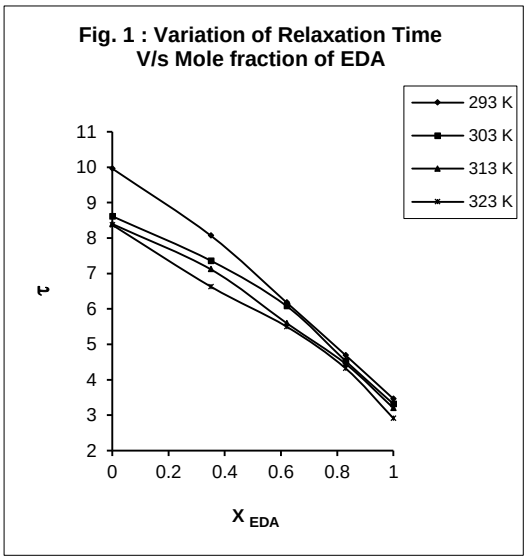
$$\eta = \left(\frac{hN}{V}\right).\exp\left(\frac{\Delta F_\eta}{RT}\right) \qquad [9]$$

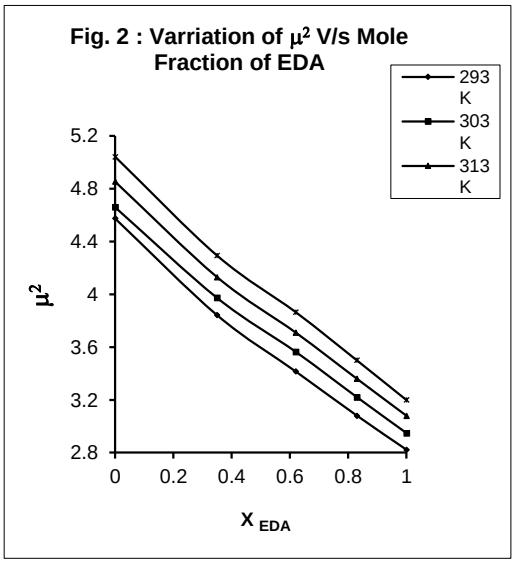
and $$\Delta F_\eta = \Delta H_\eta - T\,\Delta S_\eta \qquad [10]$$

where *V* is molar volume, η is the viscosity of the pure solvent and *K* is Boltzmann's constant other symbols have their usual meaning.

5. RESULT AND DISCUSSION:

The values of dielectric constant ($\in'$), dielectric loss($\in''$) and relaxation time (τ) for different weight fraction of solute of Iso-Amyl alcohol, ethylenediamine and their binary mixtures in 1,4-dioxan at different temperatures are shown in table 1





The values of relaxation time are observed to decrease systematically with increase in temperature from 20°C to 50°C for pure components as well as for binary mixtures. This may be due to increase in molar volume of the solute also due to the increase in the size of dipole with increase in temperature. Similar result has been predicted by Rajesh et al.[1] Fig. 1 shows variation of relaxation time (τ) with increase in the mole fraction of EDA. The relaxation time varies non-linearly with increase in mole fraction of EDA at all temperature. The non-linear variation of relaxation time shows the presence of solute – solute molecular association in the mixture.(8-9)

Fig. 2 shows non-linear variation of μ^2 with mole fraction of *EDA*. The deviation from linearity of μ^2 may be attributed to the presence of solute-solute molecular association through hydrogen bonding.(14,15)

The energy parameters ($\Delta F_\tau, \Delta H_\tau$ and ΔS_τ) for dielectric relaxation process and the energy parameters ($\Delta F_\eta, \Delta H_\eta$ and ΔS_n) for viscous flow process have been compared as shown in table 2. From table it is found free energy of activation increases with increase in temperature. With increase in temperature, the thermal agitation increases and dipole requires more energy to be an active. It is also found that free energy of activation (ΔF_τ) for dielectric relaxation process is less than the free energy of activation (ΔF_η) for the viscous flow process. This may be explained on the basis that dielectric relaxation process involves the rotation of the molecules whereas in the viscous flow process, the rotation as well as the translation motion of the molecules is involved. Similar kind of results have been shown by several research workers. (1,11) The enthalpy of activation (ΔH_η) for viscous flow process is greater than the enthalpy of activation (ΔH_τ) for dielectric relaxation process The entropy of activation (ΔS_τ) for dielectric relaxation process is found to be negative, indicating cooperative environment of the system.(14,23) Again negative entropy of activation suggest activated state is more ordered than normal state of system. (24)

6. CONCLUSION:

- The non-linear variation of relaxation time suggests the solute-solute molecular association in the mixture.
- Solute-solvent interaction has been concluded from temperature dependent of dipole moment values in pure *IAA*, *EDA* and their binary mixtures.
- Studies of thermodynamic parameters suggest that, the dielectric process involves rotation of molecules where as viscous flow process involves rotational as well as translational motion of molecules.
- Negative values of entropy of activation for dielectric relaxation process indicates that, the activated state is more ordered than normal state of molecules.

REFERENCES:

1. Rajesh Kumar, Nagesh Thakur, Sharma D.R. Rangra Virsing and Nainjeet Singh Negi(2005),*Indian J. Phys.*, 79(12), 1415-1418.
2. Rana V.A. and Vyas A.D (2004),.*Indian J. Phys.*, 78(B), 165-169.
3. Gupta K.K., Bansal A.K., Singh P.J. and Sharma K.S(2005).*Indian J. Phys.*, 79(2), 147-152.
4. Nimkar M.J., Rekha Pande and Kalamse G.M.,(2004),*Int. J. Chem. Sci.* 2(2), 251-258.
5. Vyas A.D., Vashisth V.M., Rana V.A. and Thaker N.G. (1994) *J. Mol. Liq.*,62,221-226.
6. Rewar G.D. and Bhatnagar D.(2001), *Indian J. of Pure and Applied Phys.*, Vol. 39, 707-713.
7. Gopal Krishna K.V.,(1957)*Trans Faraday Soc.*, 53, 767.
8. Sharma A. and Sharma D.R., (Nov. 1993) *Indian J. Pure and Applied Phys.*, Vol. 31,, 841-844.
9. Gupta K.K. and Singh P.J.(2003). *Indian J. Phys.*, 77B(6), 673-676.
10. Vyas A.D. and Rana V.A(2001),,*Indian J. Pure and Applied Phys.*, Vol. 39, 316-320.
11. Rangra Virsingh and Sharma D.R.(2004),,*Indian J. Phys.*, 78B(1), , 111-114.
12. Heston (Jr.), Franklim W.H. and Hennelly, (1950)*J. Am. Chem. Soc.*, 72, 3443.
13. Hill N.E., Vaughan W.E., Price A.H. and Devies M. (1969)*'Dielectric properties and molecular behaviour,'* Van Nostrand, London, pp.71 and 253.
14. Gupta K.K., Bansal A.K., Singh P.J., and Sharma K.S.(Jan. 2003), *Indian J. of Pure and Applied Phys.*,Vol.41, 57-63.
15. Singh P.J. and Sharma K.S.(1996),,*Indian J. of Pure and Applied Phys.*,Vol.34, 1.
16. Singh P.J. and Sharma K.S.,(1993), *Indian J. of Pure and Applied Phys.*,Vol.31, 721-726.
17. Khatri M. and Gandhi J.M.(1985)*J. Mol. Liq.*, 30, 63.
18. Khomeshara S.M. and Sisodia M.L.(1979),*Adv. Mol. Relax Int. Process*, 15, , 213.
19. Yadav J.S. and Gandhi J.M, (1993),*Indian J. of Pure and Applied Phys.*,Vol.31, 489
20. Sengwa R.J., Madhvi and Abhilasha, *Microwave and Optoelectronics*,(2004),Anamaya Pub., New Delhi, 104-109.
21. Nimkar M.J.(May 2002) *Thesis submitted to S.R.T.M. University, Nanded,(M.S.)* Chap.4,
22. Hill N.E., Vaughan W.E., Price A.H. and Devies M.,(1969) *'Dielectric properties and molecular behaviour,'* Van Nostrand, London, pp.393-396.
23. Rewar G.D. and Bhatanagar D.(2001), *Indian J. Phys.*, 75A (5), 541-546.
24. Branin F.H. and Smyth C.P.,(1952),*J. Chem. Phys.*, 20, 1121.
25. Pawar V.P., Raju G.S. and Mahrotra S.C.,(2002),*Pramana*, Vol. 59, 4, 693-699.

Table – 1:The values of dielectric constant ($\in'$), dielectric loss($\in''$) and relaxation time (τ) for different weight fraction of solute of Iso-Amyl alcohol, ethylenediamine and their binary mixtures in 1,4-dioxan at different temperatures.

Temperature →		293°K			303°K			313°K			323°K		
Solute %	Wt. Fraction	$\in'$	$\in''$	τ ps	$\in'$	$\in''$	τ ps	$\in'$	$\in''$	τ ps	$\in'$	$\in''$	τ ps
IAA 100%	0.0373	2.862	0.253	9.96	2.738	0.217	8.61	2.655	0.175	8.40	2.602	0.147	8.37
	0.0727	2.919	0.329		2.887	0.285		2.767	0.234		2.710	0.208	
	0.1050	3.018	0.405		2.856	0.338		2.826	0.302		2.796	0.269	
	0.1356	3.087	0.479		3.052	0.442		3.018	0.392		2.887	0.332	
IAA (65%) *+EDA* (35%)	0.0388	2.826	0.264	8.07	2.767	0.232	7.36	2.738	0.199	7.12	2.655	0.179	6.63
	0.0748	2.950	0.374		2.887	0.332		2.856	0.294		2.796	0.257	
	0.1082	3.087	0.470		3.066	0.429		3.018	0.388		2.950	0.343	
	0.1392	3.233	0.556		3.196	0.509		3.160	0.469		3.087	0.421	

IAA (38%) +*EDA* (62%)	0.0378 0.0765 0.1105 0.1421	2.950 3.018 3.393 3.478	0.325 0.374 0.604 0.647	6.18	2.826 2.919 3.311 3.435	0.278 0.317 0.534 0.602	6.08	2.796 2.887 3.196 3.393	0.241 0.282 0.458 0.548	5.60	2.767 2.858 3.160 3.311	0.209 0.253 0.415 0.489	5.50
IAA (17%) +*EDA* (83%)	0.0406 0.0780 0.1126 0.1447	2.856 3.087 3.160 3.478	0.273 0.368 0.437 0.554	4.69	2.862 3.018 3.123 3.393	0.238 0.328 0.394 0.486	4.53	2.796 2.919 3.087 3.311	0.205 0.284 0.352 0.433	4.45	2.767 2.887 3.052 3.233	0.182 0.253 0.323 0.385	4.32
EDA (100%)	0.0417 0.0801 0.1154 0.1482	2.767 3.087 3.338 3.537	0.271 0.335 0.384 0.438	3.46	2.738 3.065 3.312 3.478	0.192 0.304 0.363 0.386	3.32	2.710 3.018 3.286 3.393	0.170 0.273 0.334 0.340	3.20	2.682 2.975 3.258 3.367	0.178 0.223 0.286 0.319	2.91

Table –2. The values of free energy of activation (ΔF_τ, ΔF_η), enthalpy of activation (ΔH_τ, ΔH_η) and entropy of activation (ΔS_τ, ΔS_n) for IAA, EDA and their binary mixtures in 1,4-diaxon at different temperatures.

Solute %	Temp. ^oK	ΔF_τ K cal/mole	ΔH_τ K cal/mole	ΔS_τ cal/mole	ΔF_η K cal/mole	ΔH_η K cal/mole	ΔS_n cal/mole
IAA (100%)	293 303 313 323	2.39 2.41 2.49 2.59	0.637	-5.98 -5.85 -5.92 -6.02	3.231 3.232 3.225 3.167	4.033	2.738 2.644 2.581 2.680
IAA (65%) +*EDA* (35%)	293 303 313 323	2.27 2.31 2.38 2.44	0.233	-6.95 -6.85 -6.86 -6.83	3.231 3.232 3.225 3.167	4.033	2.738 2.644 2.581 2.680
IAA (38%) +*EDA* (62%)	293 303 313 323	2.11 2.20 2.24 2.32	0.252	-6.34 -6.43 -6.35 -6.40	3.231 3.232 3.225 3.167	4.033	2.738 2.644 2.581 2.680
IAA (17%) +*EDA* (83%)	293 303 313 323	1.95 2.02 2.09 2.16	0.307	-5.60 -5.65 -5.69 -5.74	3.231 3.232 3.225 3.167	4.033	2.738 2.644 2.581 2.680
EDA (100%)	293 303 313 323	1.78 1.83 1.89 1.91	0.429	-4.597 -4.630 -4.667 -4.585	3.231 3.232 3.225 3.167	4.033	2.738 2.644 2.581 2.680