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Microwave assisted co-operative dynamics and structural variations in chlorobenzene-acetonitrile solutions

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Abstract

Molecular interactions between CBZ-ACN at 8.845 GHz of microwave frequency region confer structural behavior of molecules such that either monomers or multimers are present in the agreed binary mixtures. Effect of microwave frequency on molecular interactions and hydrogen bonding between C≡N (nitrile) molecule and Cl (chlorine) molecule of CBZ and ACN binary solutions has been studied using X-band microwave technique at 301ºK. Co-operative dynamics and hydrogen bonding between nitrile and chlorine group molecules has been thoroughly explicated thereby obtaining static dielectric constant, excess permittivity, Kirkwood correlation factor using Luzar model and Bruggeman factor.

Keywords: Static dielectric permittivity; Excess permittivity; Kirkwood correlation factor; Luzar model; Bruggeman factor; X-band technique

Introduction

Structural variations and molecular interactions in binary liquids are detected by a responsive tool such as dielectric microwave X-band technique (Sisodia, 2005; Hengcharoena *et al.,* 2010; Birajdar *et al.,* 2021; Thakur and Sharma, 2003; Murthy *et al.,* 2003; Birajdar and Suryawanshi, 2021); it plays a significant role in perceptive of molecular assets and intermolecular exchanges in binary liquids. Study of molecular structure at different concentrations and investigation of hydrogen-bonded compounds such as polar and non-polar solvent under high frequency provides valuable information regarding molecular complex formation in binary solution. Also the molecular association and dissociation between hetero molecular entities such as CBZ-ACN is to be identified by obtaining the dielectric parameters of the liquids which reveals the effect of orientation and rotation of molecules. The dielectric properties are dependent on the composition, different external factors like temperature, humidity, intensity and frequency of changing electric field (Jia *et al.,* 2009).

Acetonitrile is a simple organic colorless nitrile compound. It is a polar, aprotic solvent and miscible in water, is abbreviated as methyl cyanide has chemical formula as [CH_3CN] and has been used in synthesis and purification of butadiene in refineries, in laboratory as a medium-polarity solvent. It is widely used in battery applications because of its relatively high dielectric constant and ability to dissolve electrolytes and it is used as a solvent for the manufacture of pharmaceuticals and photographic film in the industries (McConvey *et al.,* 2012; https://en. wikipedia. org/wiki/Acetonitrile).

Chlorobenzene (CBZ) is colorless, flammable liquid, aromatic organic compound, non-associative and chlorine group molecule with chemical formula [C_6H_5Cl].

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It is widely used as common solvent and an intermediate for other chemicals manufacturing such as in the production of commodities that is in herbicides, dyestuffs and rubber (https://en.wikipedia.org/wiki/Chlorobenzene).

Materials and methods

Acetonitrile (HPLC grade, Sai Pharma, Pune) and Chlorobenzene, (AR grade, s d fiNE-Chem Limited, Bombay) were used without further purification. The dielectric parameters were obtained at 8.845 GHz of frequency by means of X-band microwave technique as shown in figure 1. Analysis of raw data with procedure was systematically explicated in earlier articles (Sisodia, 2005; Hengcharoena *et al.,* 2010; Birajdar *et al.,* 2021; Thakur and Sharma, 2003; Murthy *et al.,* 2003; Birajdar and Suryawanshi, 2021).

The relative permittivity of binary liquid mixture is expressed (Sisodia, 2005) as,

$$\varepsilon = \varepsilon' - j\varepsilon'' \quad (2)$$

where, ε is the relative permittivity, ε' is the relative real permittivity and ε" is relative loss.

A graph is plotted between several mean values of ρ_n versus n values; slope of this graph provides value of $\frac{d\rho_{mean}}{dn}$ to eliminate the losses (Birajdar and Suryawanshi, 2017; Nimkar *et al.,* 2004). The static dielectric permittivity and loss is calculated by using the following equations as (Sisodia, 2005),

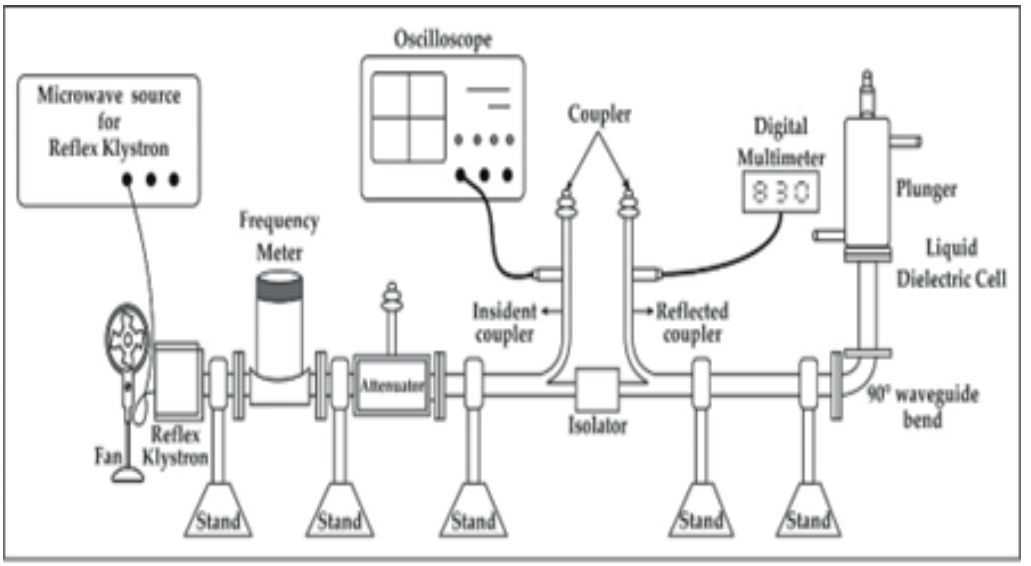

Fig. 1. Experimental setup of X-Band microwave technique with liquid dielectric cell.

Results and discussion

Static dielectric constant

Static dielectric constant and other parameters are obtained using X-band microwave technique with liquid dielectric cell. The experimental values of forward current I_f and reflected current I_r are used to calculate ε' and ε" indirectly using following equation (Sisodia, 2005) as,

$$\mathrm{VSWR} = \frac{(I_f + I_r) + 2\sqrt{I_f I_r}}{I_f - I_r} \quad (1)$$

$$\varepsilon' = \left(\frac{\lambda_o}{\lambda_c}\right)^2 + \left(\frac{\lambda_o}{\lambda_d}\right)^2 \quad (3)$$

$$\varepsilon'' = \frac{2}{\pi}\left(\frac{\lambda_o}{\lambda_d}\right)^2 + \left(\frac{\lambda_g}{\lambda_d}\right)^2 \frac{d\rho_{mean}}{dn} \quad (4)$$

where, **ε'** is dielectric constant, ε" is dielectric loss, λ_o is free space wavelength, λ_d is wavelength in the dielectric cell, λ_g is

Table I. Static dielectric constant (ε'), dielectric loss (ε'') (Birajdar and Suryawanshi, 2019; Birajdar et al., 2021), excess permittivity ($ε'^{E}$), Kirkwood correlation factor (g^{eff}, g_1, g_2) and Bruggeman factor (f_B) at 301° K.

	Dielectric Parameters						
V_{ACN}	ε'	ε''	$ε'^{E}$	g^{eff}	g_1	g_2	f_B
0.0	4.924	1.068	0.000	0.609	------	1.0000	1.000
0.2	9.552	2.637	0.442	0.562	1.0196	1.0190	0.863
0.4	16.109	3.332	-1.204	0.650	1.0277	1.0329	0.653
0.6	20.894	8.864	-0.264	0.651	1.0339	1.0435	0.498
0.8	28.267	5.495	-1.097	0.735	1.0387	1.0519	0.245
1.0	33.549	30.669	0.000	0.760	1.0427	------	0.000

guided wavelength, λ_c is cut-off wavelength which is equal to 2a, as 'a' is width of waveguide.

It is clear that static dielectric constant affected due to heterogeneous interactions between CBZ-ACN binary solutions which may create structural variations in binary solutions (Lide, 2007; Birajdar *et al.,* 2020), variations in dielectric constant, excess permittivity, Bruggeman factor and Kirkwood correlation factor are tabulated in Table I.

Excess permittivity

Excess permittivity is a dielectric parameter, provides information concerning interaction between constituents of mixture (Joshi *et al.,* 2016). Excess permittivity $ε'^{E}$ is defined as (Sivagurunathan, 2006),

$$ε'^{E} = (ε')m - [(ε')_1 \ V_1 + (ε')_2 (1-V_1)] \qquad (5)$$

where, the subscript m, 1 and 2 have their usual meanings, v_1 is volume fraction of solute. Excess permittivity values for CBZ-ACN binary mixtures are negative above 0.4 V_{ACN} such that CBZ acts as a structure breaker for ACN (Mahajan and Kumbharkhane, 2012) thereby indicating strong intermolecular interactions (Birajdar *et al.,* 2022; Carey and Sundberg, 1990; Zeberg-Mikkelsen and Andersen, 2005). Peak negative value for CBZ-ACN is at 0.4 volume concentration.

Kirkwood correlation factor

Kirkwood provides information concerning dipole-dipole orientation. Effective Kirkwood correlation factor g^{eff} of unlike molecules in binary mixture is calculated from the modified Kirkwood equation (Birajdar *et al.,* 2021; Joshi and Kumbharkhane, 2012),

$$\frac{(ε'_m-ε'_{\infty m})(2ε'_m+ε'_{\infty m})}{ε'_m(2ε'_{\infty m}+2)^2} = \frac{4\pi N}{9kT}\left[\frac{\mu_1^2\,\rho_1}{M_1} V_1 + \frac{\mu_2^2\,\rho_2}{M_2}(1-V_1)\right] \times g^{eff} \qquad (6)$$

where, g^{eff}, $ε'_m$, μ_1, μ_2, ρ_1, ρ_2, M_1, M_2, N, K, T has their usual meanings and V_1 is volume fraction of solute.

Effective Kirkwood correlation factor 'g^{eff}' for ACN and CBZ at 301° K is found to be 0.76, 0.60 respectively. It is seen that for all concentrations of binary mixtures, g^{eff} value is < 1, close to unity at 301° K which indicates the insufficient interaction with anti-parallel orientation of electric dipoles (Joshi and Kumbharkhane, 2012; Sengwa *et al.,* 2009; Kadam *et al.,* 2013). The g^{eff} values increases with increase in ACN in CBZ, confirms strong interaction in ACN rich region and weak interactions in CBZ region which is indication of deviation from unity (Shere, 2020; Ingole *et al.,* 2018). Luzar model reveals the effect of hydrogen bonding relationship in dipoles. It is not feasible to separate the average correlation factors g_1 and g_2 from single value of dielectric constant. So that the separation of g_1 and g_2 cross correlation terms must be taken into concern thereby applying Kirkwood-Froehlich theory to the binary solutions containing two unlike molecules (Luzar, 1990).

$$g_1 = 1 + Z_{11}\cos\Phi_{11} + Z_{12}\cos\Phi_{12}\left(\frac{\mu_2}{\mu_1}\right) \qquad (7)$$

$$g_2 = 1 + Z_{21}\cos\Phi_{21}\left(\frac{\mu_1}{\mu_2}\right) \qquad (8)$$

Kirkwood correlation factors for separate class i= 1 and 2 are modified. The correlation factors g_1 and g_2 are obtained by using the following equations (Sudo *et al.,* 2007),

where, $Z_{11} = 2\langle n^{11}{}_{HB}\rangle$, $Z_{12} = 2\langle n^{12}{}_{HB}\rangle$ and $Z_{21} = 2\langle n^{21}{}_{HB}\rangle$ $(1-V_{ACN}) / V_{ACN}$ are the average number of hydrogen bonds

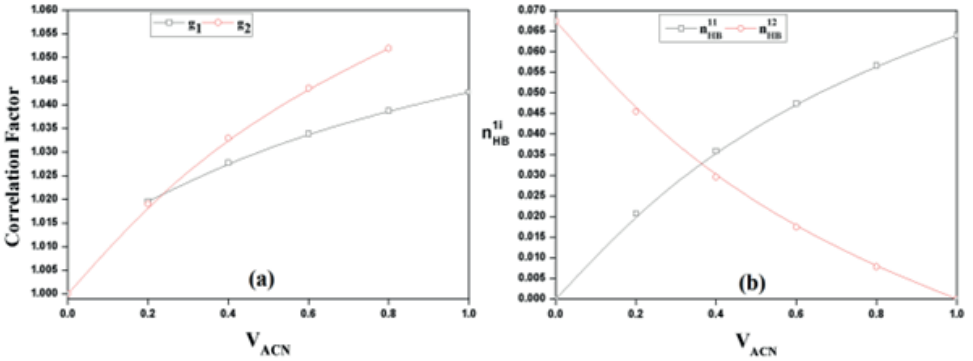

Fig. 2(a). Plots of correlation factor (g1 and g2) and (b) Plot of average number of hydrogen bonds per unit volume vs. VACN

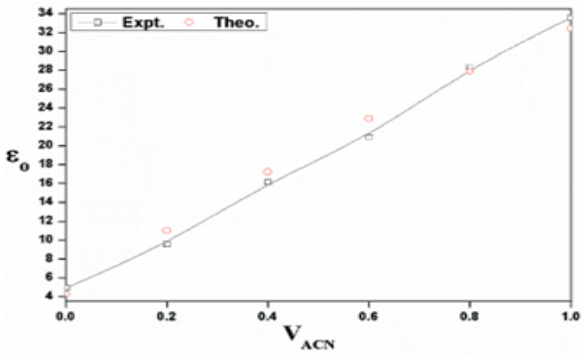

Fig. 3. Comparison of experimental and theoretical values of εo vs. VACN

with ACN-ACN and ACN-CBZ pairs respectively. V_{ACN} and V_{CBZ} are the volume fraction of ACN and CBZ respectively. Φ_{11} and Φ_{12} are the angles between the neighboring dipoles of ACN and CBZ molecules.

As shown in figure 2 (a), the values of correlation factor g_1 and g_2 increases with increasing V_{ACN} and it is clear that the value of $n^{11}{}_{HB}$ decreases and $n^{12}{}_{HB}$ increases with increasing V_{ACN} as shown in figure 2 (b) (Luzar, 1990; Sudo *et al.,* 2007; Kumbharkhane *et al.,* 2013). Average number of hydrogen bonds ($n^{11}{}_{HB}$) and ($n^{12}{}_{HB}$) per CBZ molecule for 1i pairs (i =1 or 2) has been calculated by the following equation (Luzar, 1990),

$$n_{HB}^{1i} = n_{HB}^{1i} n_{1i} \omega^{1i} / n_1 \qquad (9)$$

where $\omega^{1i} = 1/[1+ \alpha^{1i} \exp(\beta E^{1i})]$ is the possibility of creation of bond between ACN and CBZ. n_1 is the number density of ACN molecules, $\beta = 1/kT$, and α^{1i} are the statistical volume ratios of two sub-volumes of the phase space related to the non hydrogen-bonded and hydrogen bonded pairs. These hydrogen bonded pairs have two energy levels, E^{11} and E^{12}, for 11 and 12 pair created bonds respectively. Values of ($n^{11}{}_{HB}$) and ($n^{12}{}_{HB}$) depend on the number of densities of the hydrogen-bonded pairs between ACN and CBZ (n_{12}) and between ACN molecules ($n_{11} = 2n_1 - n_{12}$) respectively. These are calculated during the formation of ACN-ACN (11 pair) and ACN-CBZ (12 pair) (Rewar and Bhatnagar, 2002).

Luzar model provides qualitative values of dielectric constant of ACN-CBZ binary mixtures as shown in figure 3 and the probable values of molecular parameters with which static dielectric constant values are in good agreement with experimental values and are reported in Table II.

Table II. Molecular parameters used in computation of static dielectric constant (εo) at 301°K.

Molecular parameters	
Effective Dipole moment[a] of ACN	3.92
Effective Dipole moment[a] of CBZ	1.50
Polarizability[b] of ACN	1.6
Polarizability[b] of CBZ	7.8
Binding energy[c] of ACN-ACN	-1
Binding energy[c] of ACN-CBZ	-0.5
Enthalpy[c] of ACN-ACN	45
Enthalpy[c] of ACN-CBZ	35
Number of Hydrogen Bond	1

[a]Unit : Debye; [b]Unit : A^{03}; [c]Unit: KJ/mol

Bruggeman factor

Bruggeman explores the information regarding the static permittivity of the liquid and is given by the relation as (Puranik *et al.,* 1994),

The Bruggeman equation has been modified for binary liquid mixtures (Puranik *et al.,* 1994) as,

$$f_B = \left[\frac{(\varepsilon'_m - \varepsilon'_1)}{(\varepsilon'_2 - \varepsilon'_1)}\right]\left[\frac{\varepsilon'_2}{\varepsilon'_m}\right]^{\frac{1}{3}} = 1 - V_2 \qquad (10)$$

where, f_B is the Bruggeman factor, ε'_m, ε'_1 and ε'_2 have their usual meanings, V_2 is the volume fraction of solvent. In modified Bruggeman equation the volume fraction (V_2) is changed by a factor [a-(a-1) V_2] of the mixture where 'a' is the interaction parameter.

$$f_B = \left[\frac{(\varepsilon'_m - \varepsilon'_1)}{(\varepsilon'_2 - \varepsilon'_1)}\right]\left[\frac{\varepsilon'_2}{\varepsilon'_m}\right]^{\frac{1}{3}} = 1 - [a - (a-1)V_2]V_2 \qquad (11)$$

The value of interaction parameter 'a' for CBZ-ACN is found to be 0.55 at 301° K which suggests increased effective dipoles with strong intermolecular interactions (Birajdar *et al.,* 2021) as shown in figure 4.

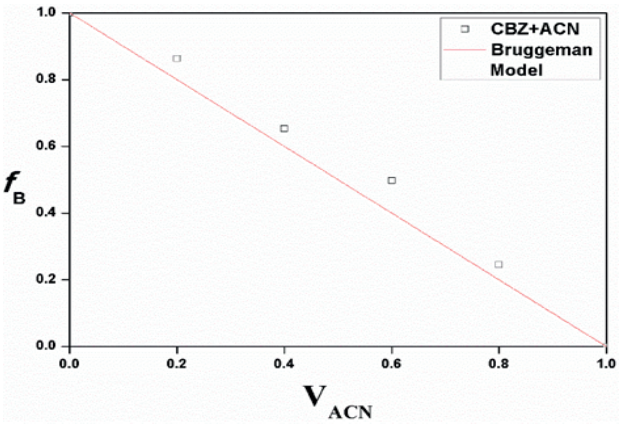

Fig. 4. Variation in Bruggeman factor with VACN at 301° K.

Conclusion

The experimentally obtained values of all binary solutions provide qualitative research information regarding static dielectric constant, excess permittivity, Kirkwood correlation factor and Bruggeman factor. In case of excess permittivity the values are negative for CBZ-ACN with an indication of strong intermolecular interaction. In Kirkwood correlation factor the dipoles are oriented in antiparallel manner. Luzar model reveals that the theoretical and experimental static dielectric constant values are well in accordance with each other. The Luzar model provides a theoretical basis for the computation of molecular parameters. Bruggeman factor values for all solutions are less than one suggests increased effective dipoles with strong intermolecular interactions.

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References

Birajdar SS and Suryawanshi DB (2017), Molecular and Structural Interaction Study of Chlorobenzene-Xylene Binary Mixture Using X-Band Dielectric Technique, *IJIRSET.* **6**(12): 22695-22698.

Birajdar SS and Suryawanshi DB (2019), Dielectric Properties of Chlorobenzene with Acetonitrile Using X-Band Microwave Dielectric Technique, *Research Journey.* **93**: 51-54.

Birajdar SS, Suryawanshi DB and Kumbharkhane AC (2020)**,** Dielectric Relaxation Behaviour of n-Butyl Acetate-Xylene Mixtures using Time Domain Reflectometry ***In:*** Proc. of KSTA Sponsored International Conference on Physics and Allied Sciences, Bidar, India, pp 85-90,

Birajdar SS, Vagshette ND, Birajdar Shilpa S, Suryawanshi DB and Lathi AR (2021), Structural characterization of acetonitrile-xylene binary mixtures at 301° K using high frequency X-band technique, *VIIRJ.* **12 (1)**: 125-130.

Birajdar SS and Suryawanshi DB (2021), Microwave dielectric relaxation study of pure liquids and binary mixtures, *AIIRJ. Special issue* **88**: 213-216. DOI: org/10.1016/j.saa.2017.02.023

Birajdar SS, Khandekar MS and Suryawanshi DB (2021), Comparative dielectric study of acetonitrile, chlorobenzene and xylene binary solutions using microwave technique, *VIIRJ.* Special issue part **13**: 2961-2967.

Birajdar SS, Suryawanshi DB, Deshmukh AR, Shinde RV, Ingole SA and Kumbharkhane AC (2021), Dielectric relaxation behaviour of ethyl acetate-xylene mixtures using time domain reflectometry, *Physics & Chemistry of Liquids* **59**(4): 503-511. DOI: org/10.1080/00319104.2020.1743702

Birajdar SS, Deshmukh AR, Suryawanshi DB and Kumbharkhane AC (2021), Molecular interaction studies of isopropyl acetate-xylene mixture using dielectric relaxation approach, *IJCA.* **60 A**: 72-79.

Birajdar SS, Kumbharkhane AC, Hallale SN, Hudge PG and Suryawanshi DB (2022), Thermodynamic and dielectric properties of Cyclohexanol-Xylene binary

mixtures using dielectric spectroscopy, *Polycyclic Aromatic Compounds.* **21:** 1-9. DOI: 10.1080/ 10406638. 2022.2032767.

Carey FA and Sundberg RJ (1990), Advanced Organic Chemistry-Part A: Structure and Mechanisms, 3rd Ed., Plenum Press, New York.

Hengcharoena T, Eaiprasertsaka K and Fuangfoong M (2010), Microwave Dielectric Measurement of Liquids by using Waveguide Plunger Technique ***In:*** 2nd International Science, Social Science, Engineering and Energy Conference: Engineering Science and Management, Nakhonphanom, Thailand, pp 270-274.

Ingole SA, Deshmukh AR, Shinde RV and Kumbharkhane AC (2018), Dielectric relaxation study of aqueous tetraethylene glycol using time domain reflectometry technique in the frequency range 10 MHz to 50 GHz, *J. Mol. Liquis.* **272**: 450-455. DOI: org/10.1016/j.molliq. 2018.09.108

Jia G, Huang K, Yang L and Yang X (2009), Composition-Dependent Dielectric Properties of DMF-Water Mixtures by Molecular Dynamics Simulations, *Int. J. Mol. Sci.* **10**: 1590-1600.

Joshi YS and Kumbharkhane AC (2012), Study of dielectric relaxation and hydrogen bonding in water +2 butoxyethanol mixture using TDR Technique, *Fluid Phase Equilibria.* **317**: 96-101 DOI: org/10.1016/j .fluid.2012.01.005.

Joshi YS, Kanse KS, Rander DN and Kumbharkhane AC (2016), Dielectric relaxation and molecular interaction study of aqueous amides, *IJPAP*. **54**: 621-628.

Kadam SS, Hudge PG, Suryawanshi DB and Kumbharkhane AC (2013), Dielectric relaxation study of 2 and 3-chloroaniline and 2 and 3-methoxyaniline with 1,4-dioxane mixtures using time domain technique, *Journal of Molecular Liquids* **177**: 426-431.

Kumbharkhane AC, Joshi YS, Mehrotra SC, Yagihara S and Sudo S (2013), Study of hydrogen bonding and thermodynamic behavior in water–1, 4-dioxane mixture using time domain reflectometry, *Physica B.* **421**: 1-7. DOI: org/10.1016/j.physb.2013.03.040

Lide DR (2007), CRC handbook of chemistry and physics. 87th Ed. Boca Raton (FL) Taylor and Francis.

Luzar A (1990), Dielectric behavior of DMSO-Water mixture, A hydrogen bonding model, *J. Mol. Liquids.* **46**: 221-238.

Mahajan GR and Kumbharkhane AC (2012), Dielectric relaxation and hydrogen bonding behavior of amides in non-polar solute using picoseconds time domain technique, *International Journal of Bioscience, Biochemistry and Bioinformatics.* **2**(2): 117-121.

McConvey IF, Woods D, Lewis M, Gan Q and Nancarrow P (2012), Org. Process Res. Dev. **16**: 612−624.

Murthy MBR, Dyasagar BS and Patil RL (2003), Measurements on polar liquids at a microwave frequency evaluation of molecular parameters-a new method, *Journal of Physics.* **18**(4): 725-727.

Nimkar MJ, Pande R and Kalamse GM (2004), Dielectric Relaxation and Thermodynamic Parameters of Amines-Trigol in 1, 4 Dioxane using Microwave Technique, *Int. Journal of Chem. Sci.* **2**(2): 251-258.

Puranik SM, Kumbharkhane AC and Mehrotra SC (1994), The static permittivity of binary mixtures using an improved Bruggeman model, *J. Mol. Liquids.* **59**: 173–177. DOI: .org/10.1016/0167-7322(93)00665-6

Rewar GD and Bhatnagar D (2002), Dielectric relaxation in ternary mixtures of benzotrifluorides, *Indian J. Pure Appl. Phys.* **40**: 430-435.

Sengwa RJ, Khatri V and Sankhla S (2009), Dielectric behavior and hydrogen bond molecular interaction study of formamide-dipolar solvents binary mixtures, *J Mol. Liquids.* **144**: 89. DOI: .org/10.1016 /j.molliq. 2008.10.0

Shere IG (2020), Molecular Correlation Study of Acetonitrile and Dichloromethane Mixture at 25º C Temperature using Microwaves, *AIIRJ.* **7(3)**: 15-17.

Sisodia ML (2005), Basic Microwave Techniques and Laboratory Manual, *Newage publishers, India*.

Sivagurunathan P (2006), Dielectric Relaxation Study of Ethyl Acrylate-Alcohol Mixtures Using Time Domain Reflectometry, *Lithuanian Journal of Physics* **46**(4): 441-445.

Sudo S, Oshiki N, Shinyashiki N, Yagihara S, Kumbharkhane AC and Mehrotra SC (2007), Dielectric Properties of Ethyleneglycol-1, 4-Dioxane Mixtures Using TDR Method, *J. Phys. Chem A.* **111**: 2993-2998. DOI: org/10.1021/jp068222s

Thakur N and Sharma DR (2003), Dielectric relaxation of acetonitrile in benzene solution from microwave absorption studies, *IJPAP.* **41**: 806-809.

Zeberg-Mikkelsen CK and Andersen SI (2005), Density Measurements under Pressure for the Binary System 1-Propanol + Toluene, *J. Chem. Eng. Data.* **50**: 524-528. DOI: org/10.1021/je049685z