FULL PAPER

Relaxation Time, Excess Relaxation Time and Dipole Moment of Binary Mixture of 2,3-Dichloroaniline and 2-Methoxyethanol using Frequency Domain Reflectometer

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Abstract:

Dielectric constant (ε') and dielectric loss (ε'') of 2,3-Dichloroaniline (2,3-DCA), 2-Methoxyethanol (2-ME) and binary mixtures of 2,3-DCA+2-ME in 1,4-dioxane solutions have been measured at microwave frequency 10.985 GHz at different temperatures 20 ^{0}C, 30 ^{0}C, 40 ^{0}C and 50 ^{0}C. Standing microwave techniques and Gopala Krishna's single frequency concentration variation method have been used for above measurements. The measured values of ε' and ε'' have been used to evaluate dipole moment (μ) and relaxation time (τ). The dielectric relaxation process of binary mixtures containing 70% mole fraction of 2,3-DCA have been calculated. It is found that the dielectric relaxation process can be treated as the rate process like the viscous flow process. Nonlinear variation of relaxation time with molar concentration of 2,3-DCA in the whole concentration range of the binary mixture indicates the existence of solute-solute and solute–solvent type of molecular association was predicted. Dipole moment (μ) of 2,3-DCA and 2-ME slightly non-linearly increases with rise in temperature. Excess inverse relaxation time $(1/\tau)^{e}$ calculated at different temperatures are found to be positive. All parameters (ε'), (ε''), (τ), $(1/\tau)^{e}$ and (μ) are calculated and discussed to yield information on the dipole alignment and molecular rotation of the binary liquid mixtures. From all the derived dielectric parameters, molecular interactions are interpreted through hydrogen bonding.

Keywords: dielectric relaxation; dipole moment; binary mixture; 2,3-dichloroaniline; 2-methoxyethanol; microwave frequency

1. Introduction

Dielectric study of liquid mixtures has gained importance [1-2] because it provides one way of bringing together the molecules of different compounds and allows them to interact with one another. The forces responsible for such interactions cannot be studied when such molecules are isolated. Molecular mixtures bring about changes in thermodynamic properties like entropy, free energy and heat of mixing. Changes in physical properties like density, molar volume, refractive index, dielectric constant etc. are manifestations of intermolecular interactions in liquid mixtures [3, 4]. Dielectric investigations of solutions containing varying amounts of interacting molecules help to detect the formation and composition of complexes in them. The

present trend is of liquid mixtures leading to formation of hydrogen bonding in the system due to solute-solute interactions. Hydrogen bonding is complex in the liquid state because of the uncertainty in identifying the particular bonds and the number of molecules involved. One of the physical parameters used for conformational analysis of any resultant structure is the net dipole moment [5]. The study of dielectric dispersion and absorption of a binary liquid mixture provides a very sensitive tool for detecting molecular interactions. It has been observed that the formation of complexes or the presence of association leads to relaxation times considerably higher than those for the uncomplexed (unassociated) species. It has been shown by [6, 7] that a binary liquid mixture, in which both components are either associated or non-

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associated, shows a single relaxation time, where as two distinct relaxation times are observed in the mixtures in which one component is associated and the other is non-associated. Dielectric dispersion studies of polar liquids such as alcohols, aniline and their binary mixtures were carried out to determine the nature of interaction that exist between the molecules due to hydrogen bonding dipole moment and the relaxation behavior phenomena. Dielectric spectroscopy is sensitive to changes in bonding between different species of liquids in a liquid-liquid binary or tertiary systems even to weak hydrogen bonding. Dipole moments are determined for the polar solute system diluted in non-polar solvent benzene to minimize the dipole-dipole interaction. The dielectric behavior of some hydrogen bonded polar liquid mixtures was studied [8]. The liquid mixtures in the present study are useful for hydrogen bonding formation with liquid crystals [9] which eventually affect the dipole moment and relaxation time. The relaxation time studies are carried out [10] in the binary mixtures of isopropanol with methyl/ethyl benzoates. Dielectric study of 2,3-DCA+2-ME binary mixture has not been carried out in the past. As such it was felt that the present study provides most useful information regarding the molecular interaction and the formation of complexes in the binary mixture of 2,3-DCA+2-ME. 2,3-Dichloroaniline is used starting material for synthesis of bioactive Schiff's bases, azetidinones, thiazolidinones, pyrazolines, acetohydrazides and in coupling reactions. It is used in preparation of poly (2,3-dichloroanline-Co-anline) which control conductivity in broad range from 10^{-9} to 10^{-2} S /cm. Also, it is used in preparation in dyes, azo-dyes, isocynates and in plant protection agent [11]. 2-Methoxyethanol [12] is also called as methyl cello solve and used as a solvent for mainly different purpose, such as in nail polish remover, varnishes, dyes, resins paints, wood stain, lacquer industries, semiconductor industries, all purpose liquid cleaners and spray solutions. By varying its concentration in non-polar solvent medium 1,4-dioxane in the microwave frequency range at 10.985 GHz (X-band) by using plunger and cavity perturbation [13] methods. Dipole moment calculated using the Higasi's method [14].

2. Material and Methods

2.1. Materials 2,3-Dichloroaniline (GC Grade) was obtained from Sigma-Aldrich, Germany, 2-Methoxyethanol Sigma Aldrich USA and 1,4-dioxane (AR Grade) were purchased from M/S Sd. Fine chemical, Mumbai, India. Without further purification the two liquids 2,3-DCA+2-ME 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.

2.2. Measurement

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) having accuracy of density 0.001 gm/cm^3, repeatability 0.0005 gm/cm^3 and resolution 0.0001 gm/cm^3 [15] and viscosity measured by LVDL, V-pro II Brook field viscometer (USA) [16]. 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.The X-band microwave bench was used to measure wavelengths in the dielectric and the voltage standing wave ratio (VSWR). The dielectric constant (ε') and the dielectric loss (ε'') of dilute solutions of binary mixture of 2, 3-DCA and 2-ME in 1,4-dioxane were calculated using microwave absorption techniques [17]. All the measurements were carried out at temperatures 20^{0}C, 30^{0}C, 40^{0}C and 50^{0}C and the temperature was thermostatically controlled within $\pm$0.5^{0}C.

Following equations 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 wavelengths

63

Orbital: Electron. J. Chem. 12 (2): 62-68, 2020

in free space, 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, 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.

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

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

$$\mu^2 = \frac{9kTM}{4\pi Nd_0}\left[1+\left(\frac{dY}{dX}\right)^2\right]\frac{dX}{dW} \quad \text{.........(5)}$$

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

Where N is the Avogadro number, M is the molecular weight of polar substance, W is the weight fraction and d_o is the density of solution.

The ε' and ε'' for the binary mixture 2,3-DCA+2-ME in the 1,4-dioxane solution have been calculated using the short-circuited waveguide method [17]. 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. 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 [1] The dipole moments for pure 2,3-Dichloroaniline, 2-Methxyethanol and binary mixture of 2,3-DCA+2-ME reported in Table 1-4. Dipole moment of pure 2,3-DCA and 2-ME are found to be very near to the literature values of the dipole moment. This shows that, pure 2,3-DCA and pure 2-ME exist in the monomer form in 1,4-dioxane solution.

The excess inverse relaxation time $(1/\tau)^e$ may be evaluated for binary system in non-polar

solvent using the relation [19].

$$(1/\tau)^E = (1/\tau)_m - \left[X_1(1/\tau_1) + X_2(1/\tau_2)\right] \quad \text{..... (7)}$$

The symbol m, 1 and 2 are related to the mixture, liquid 1 and liquid 2 respectively. Information regarding the dynamics of a binary system interaction from this excess property is as follows.

Where $(1/\tau)^e$ is the excess inverse relaxation time which represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (which is the inverse of the relaxation time) from resonant spectroscopy [20]. The information regarding the dynamics of solute-solvent interaction from this excess property is as follows:

$(1/\tau)^e = 0$: There is no change in the dynamics of solute-solvent interaction.

$(1/\tau)^e < 0$: The solute-solvent interaction produces a field such that the effective dipoles rotate slowly.

$(1/\tau)^e > 0$: The solute-solvent interaction produces a field such that the effective dipoles rotate quickly i.e. the filed co-operate in the rotation of the dipoles.

3. Results and Discussion

In continuation of our research work [18], here we determined the dielectric constant (ε'), dielectric loss (ε''), relaxation time (τ), Excess inverse relaxation time $(1/\tau)^e$ and dipole moment (μ) for the binary mixture of 2,3-DCA+2-ME in 1,4-dioxane solution at 20 ^{0}C, 30 ^{0}C, 40 ^{0}C and 50 ^{0}C. For different mole fraction containing 0, 30, 50, 70 and 100 mol% of 2,3-DCA+2-ME in 1,4-dioxane solution and calculated by the method suggested [17] are reported in Table 1-4.

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. 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

64

Orbital: Electron. J. Chem. 12 (2): 62-68, 2020

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 2,3-DCA+2-ME binary mixture increase linearly with the mole fraction of 2,3-DCA ($X_{2,3-DCA}$), no molecular association can be inferred. However, if the relaxation time 2, 3-DCA+2-ME binary mixture increase non-linearly, a solute-solute type of molecular association between 2,3-DCA and 2-ME may be inferred. The variation of relaxation time (τ) versus mole fraction $X_{2,3-DCA}$ at different temperatures is shown in Figure 1.
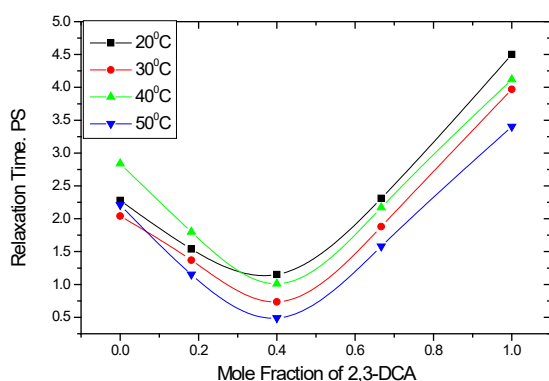

Figure 1. Relaxation time (τ) versus mole fraction of 2,3-DCA in 2,3-DCA+2-ME binary mixture in 1,4-dioxane solution at different temperatures.

The variation of the relaxation time (τ) decrease with increase in mole fraction of 2,3-DCA in 2,3-DCA+2-ME binary mixture and attains a minimum value at $X_{2,3-DCA} = 0.4$ of 2,3-DCA in the binary mixture. Then with further increase in the mole fraction of 2,3-DCA binary mixture increases in the relaxation time (τ) maximum at $X_{2,3-DCA} = 0.70$ mole fraction of 2,3-DCA in 2,3-DCA+2-ME and again increases these relaxation time which reach towards the value of pure 2,3-DCA in 1,4-dioxane solution. This behavior indicates solute-solute type of molecular association between 2,3-DCA and 2-ME. It shows that the binary mixtures of 2,3-DCA and 2-ME, 2,3-DCA exists in the dimer structure resulting because of H-bonding and dimer structure of 2,3-DCA interact with the 2-ME molecules so as to give the maximum values of

relaxation time at 70 mol% 2,3-DCA binary mixture. This type of molecular associations has been proposed in Figure 2.

The dipole moment of 2-ME binary mixture with 0.00 mole fraction of 2,3-DCA in binary mixture is found to be slightly changed with temperature and due to the π electron cloud of non-polar solvent. This could be explained on the basis of the solvent effects [13]. The change in dipole moment with temperature may be due to the stretching of the bond moment and due to the change in the bond angle. The dipole moment value of 2,3-DCA slightly non-linearly increases with the rise in temperature in 1,4-dioxane solution [21, 22]. This predicts the solute-solvent type of molecular association for 2,3-DCA in the 1,4-dioxane solution.

Solute-solute molecular association can be interpreted because of the molecule association arising due to hydrogen bonding between 2-methoxyethanol and 2,3-dichloroaniline. The hydrogen bonding δ^+ on hydrogen of hydroxyl group of 2-methoxyethanol that form hydrogen bonding with nitrogen of 2,3-dichloroaniline as shown in Figure 2.
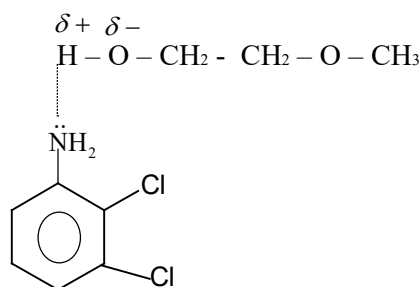
Figure 2. Solute-solute molecular association between 2,3-DCA and 2-ME.

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

The excess inverse relaxation time values are found to positive over entire concentration range of mole fraction of 2,3-DCA. The graph of excess inverse relaxation time versus mole fraction of 2,3-DCA for all temperatures are depicted in Figure 4. This suggests that the solute-solute

dimmer interaction provides a field such that the effective dipoles rotates faster i.e. the field facilitates rotation of dipoles simmer result have been already predicated [23]. The positive peak values are observed at around X=0.4 mole fraction of 2,3-DCA in 2,3-DCA+2-ME binary liquid mixture.

Table 1. Dielectric constant (ε'), dielectric loss (ε''), relaxation time (τ), excess inverse relaxation time ($1/\tau)^e$ and dipole moment (μ) of different mole fraction of 2,3-DCA in 2,3-DCA+2-ME binary mixture in 1,4-dioxane at 20 ^{0}C temperature.

Mole Fraction	Weight Fraction(W)	ε' (0.5%)	ε'' (0.1%)	τ (P.Sec)	$(1/\tau)^e$	μ D Debye
0	0.0546	2.148	0.018			
	0.1036	2.259	0.115	2.28	0	1.72
	0.1478	2.467	0.156			
	0.1878	2.710	0.202			
0.18185	0.0590	2.221	0.140			
	0.1115	2.359	0.176	1.54	0.2501	1.24
	0.1584	2.536	0.195			
	0.2006	2.540	0.199			
0.40006	0.8419	2.114	0.124			
	0.1553	2.302	0.138	1.15	0.5175	1.4
	0.2161	2.498	0.167			
	0.2688	2.512	0.185			
0.66672	0.0707	2.628	0.0893			
	0.1322	2.240	0.127	2.31	0.1386	1.34
	0.1860	2.318	0.150			
	0.2335	2.359	0.167			
1	0.0769	2.245	0.124			
	0.1428	2.380	0.188	4.50	0	1.02
	0.1999	2.420	0.193			
	0.2499	2.422	0.195			

Table 2. Dielectric constant (ε'), dielectric loss (ε''), relaxation time (τ), excess inverse relaxation time ($1/\tau)^e$ and dipole moment (μ) of different mole fraction of 2,3-DCA in 2,3-DCA+2-ME binary mixture in 1,4-dioxane at 30 ^{0}C temperature.

Mole Fraction	Weight Fraction(W)	ε' (0.5%)	ε'' (0.1%)	τ (P.Sec)	$(1/\tau)^e$	μ D Debye
0	0.0546	2.401	0.131			
	0.1036	2.628	0.162	2.04	0	1.56
	0.1478	2.769	0.205			
	0.1878	2.877	0.218			
0.18185	0.0590	2.221	0.126			
	0.1115	2.478	0.147	1.37	0.2831	1.62
	0.1584	2.654	0.189			
	0.2006	2.748	0.209			
0.40006	0.8419	2.131	0.128			
	0.1553	2.494	0.159	0.735	0.9657	1.67
	0.2161	2.604	0.169			
	0.2688	2.724	0.172			
0.66672	0.0707	2.131	0.116			
	0.1322	2.237	0.141	1.88	0.2006	1.44
	0.1860	2.478	0.171			
	0.2335	2.516	0.172			
1	0.0769	2.148	0.106			
	0.1428	2.298	0.164	4.60	0	1.49
	0.1999	2.480	0.185			
	0.2499	2.512	0.194			

66

Orbital: Electron. J. Chem. 12 (2): 62-68, 2020

Table 3. Dielectric constant (ε'), dielectric loss (ε''), relaxation time (τ), excess inverse relaxation time $(1/\tau)^e$ and dipole moment (μ) of different mole fraction of 2,3-DCA in 2,3-DCA+2-ME binary mixture in 1,4-dioxane at 40 ^{0}C temperature.

Mole Fraction	Weight Fraction(W)	ε' (0.5%)	ε'' (0.1%)	τ (P.Sec)	$(1/\tau)^e$	μ D Debye
0	0.0546	2.380	0.096			
	0.1036	2.444	0.132	2.84	0	1.42
	0.1478	2.702	0.156			
	0.1878	2.815	0.194			
0.18185	0.0590	2.120	0.087			
	0.1115	2.121	0.163	1.80	0.2271	1.38
	0.1584	2.299	0.130			
	0.2006	2.455	0.148			
0.40006	0.8419	2.125	0.124			
	0.1553	2.342	0.153	1.01	0.6900	1.32
	0.2161	2.498	0.168			
	0.2688	2.500	0.171			
0.66672	0.0707	2.238	0.112			
	0.1322	2.422	0.152	2.17	0.1953	1.58
	0.1860	2.576	0.173			
	0.2335	2.710	0.218			
1	0.0769	2.166	0.129			
	0.1428	2.278	0.178	3.70	0	1.15
	0.1999	2.422	0.197			
	0.2499	2.369	0.194			

Table 4: Dielectric constant (ε'), dielectric loss (ε''), relaxation time (τ), excess inverse relaxation time $(1/\tau)^e$ and dipole moment (μ) of different mole fraction of 2,3-DCA in 2,3-DCA+2-ME binary mixture in 1,4-dioxane at 50 ^{0}C temperature.

Mole Fraction	Weight Fraction(W)	ε' (0.5%)	ε'' (0.1%)	τ (P.Sec)	$(1/\tau)^e$	μ D Debye
0	0.0546	2.294	0.099			
	0.1036	2.389	0.118	2.21	0	1.33
	0.1478	2.684	0.134			
	0.1878	2.790	0.168			
0.18185	0.0590	2.294	0.136			
	0.1115	2.559	0.166	1.15	0.4459	1.6
	0.1584	2.684	0.192			
	0.2006	2.790	0.214			
0.40006	0.8419	2.161	0.128			
	0.1553	2.494	0.159	0.489	1.6559	1.72
	0.2161	2.604	0.169			
	0.2688	2.724	0.186			
0.66672	0.0707	2.184	0.134			
	0.1322	2.359	0.179	1.58	0.2860	1.55
	0.1860	2.536	0.169			
	0.2335	2.618	0.186			
1	0.0769	2.131	0.117			
	0.1428	2.318	0.164	3.40	0	1.18
	0.1999	2.338	0.176			
	0.2499	2.870	0.181			

$$\overset{\delta+}{H} - \overset{\delta-}{O} - CH_2 - CH_2 - O - CH_3$$
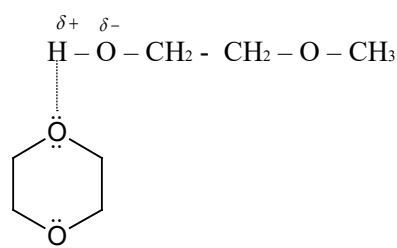
Figure 3. Solute-solvent molecular associations of 2-ME in 1,4-dioxane solution.

67

Orbital: Electron. J. Chem. 12 (2): 62-68, 2020
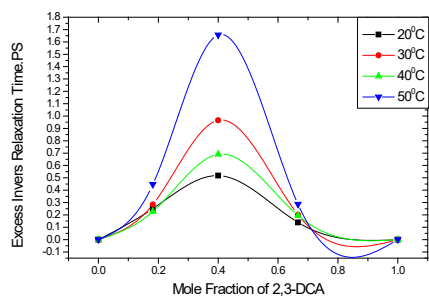
Figure 4. Excess inverse relaxation time $(1/\tau)^e$ versus mole fraction(X) of 2,3-DCA in 2,3-DCA+2-ME binary mixture in 1,4-dioxane solution at different temperatures.

4. Conclusions

The molecular association may be due to the change in molar volume or change in the effective length of the dipole involved in the orientation process between 2,3-DCA+2-ME, is maximum nearly at a 30:70 mol%, ratio respectively and then increases at higher mol% of 2,3-DCA in binary mixtures. Above results shows that the binary mixtures of 2,3-DCA+2-ME exists in the dimer structure resulting because of H-bonding and dimer structure of 2,3-DCA intract with the 2-ME molecules so as to give the maximum values of relaxation time at 70 mol% of 2,3-DCA binary mixture respectively. Relaxation time increases due to addition of -CH$_2$ group in the binary mixtures. This confirms that the relaxation time (τ) increases due to increase in carbon atoms in binary mixtures. The dipole moment is found to be slightly changed with temperature and due to the π electron cloud of non-polar solvent. This could be explained on the basis of the solvent effects. The change in dipole moment with temperature may be due to the stretching of bond moment and due to the change in bond angle. The excess inverse relaxation time $(1/\tau)^e$ are found to positive in entire concentration range of mole fraction of 2,3-DCA. This suggests that the solute-solute interaction provides a field such that the effective dipoles rotate faster i.e. under the influence of an external varying field, facilities rotation of dipoles

Acknowledgments

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68

Orbital: Electron. J. Chem. 12 (2): 62-68, 2020