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Dielectric Relaxation Spectroscopy study of binary mixture of 2, 3-Dichloroaniline and 2-Butoxyethanol in benzene solution using microwave frequency

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Abstract: Dielectric constant (ε′) and dielectric loss (ε′′) of 2,3-Dichloroaniline (2,3-DCA), 2-Butoxyethanol (2-BE) and binary mixtures of 2,3-DCA+2-BE in benzene solutions have been measured at microwave frequency 10.985 GHz at different temperatures 20^0C, 30^0C, 40^0C and 50^0C. 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 relaxation time (τ). The dielectric relaxation process of binary mixtures containing 50% 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. Non-linear 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 intermolecular association were predicted at different temperatures are found to be negative.

Key words: Dielectric relaxation time, Binary mixture, 2,3-Dichloroaniline, 2-Butoxyethanol, Microwave frequency.

INTRODUCTION

2,3-Dichloroaniline (2,3-DCA) is a amber to brown liquid solution, it is toxic by skin absorption and by inhalation it produces toxic oxides of nitrogen during combustion. 2,3-Dichloroaniline is used as an 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 [1]. 2-Butoxyethanol is an important colorless liquid with a mild order2-BE is used as a solvent for resins, varnishes, lacquer industries, enamels and all-purpose liquid cleaners [2]. It is possible to prepare binary mixture of 2,3-DCA and 2-BE having dielectric constant value in between that of 2,3-DCA and 2-BE. This motivates the authors to undertake the experimental work concerned with the dielectric relaxation process in binary mixtures of 2,3-DCA and 2-BE so as to understand the intermolecular association in the whole concentration range of 2,3-DCA in the binary mixture.

When polar molecules are subjected to electromagnetic waves in microwave frequency region, they absorb considerable microwave energy thereby perturbing dipole moment of molecules due to intermolecular rotations. The study of dielectric relaxation of polar liquids in non-polar solvents from the microwave absorption studies give valuable information about various types of the intermolecular associations present in the solutions as microwaves can detect weak intermolecular interactions [3-7]. The present investigation is concerned with the study of dielectric relaxation of binary mixtures of 2,3-DCA and 2-BE in the whole concentration range of 2,3-DCA in the binary mixtures using standard microwave standing wave techniques and single frequency concentration variation method of Gopala Krishna [8]. Measurements have been made for binary mixture of different mole fraction of 2,3-DCA+2-BE (0.0, 0.2646, 0.5191, 0.7640 and 1.0) at different temperatures 20^0C, 30^0C, 40^0C and 50^0C. 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 intermolecular associations have been proposed for 2-BE and 2,3-DCA in benzene solution.

EXPERIMENTALS DETAILS

Materials: 2,3-Dichloroaniline (GC Grade) was obtained from Merck-Schuchardt, Germany, 2-Butoxyethanol Sigma Aldrich USA and benzene (AR Grade) were purchased from M/S Sd. Fine chemical, Mumbai, India. Without further purification the two liquids 2,3-DCA+2-BE 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. 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 [3,9] and viscosity by LVDL, V-pro II Brook field viscometer (USA) [10]. 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-BE in benzene were calculated using microwave absorption techniques of Heston *et.al* [11]. All the measurements were carried out at temperatures 20^0C, 30^0C, 40^0C and 50^0C and the temperature was thermostatically controlled within $\pm 0.5^0$C.

RESULTS AND DISCUSSION

In continuation of our research work [12-13] here we determined the dielectric constant (ε'), dielectric loss (ε'') and relaxation time (τ) for the binary mixture of 2, 3-DCA+2-BE in benzene solution at

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20^0C, 30^0C, 40^0C and 50^0C. For different mole fraction containing 0, 30, 50, 70 and 100 mol % of 2,3-DCA+2-BE in benzene solution and calculated by the method suggested by Heston *et al.*[11]

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 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.

The relaxation time (τ) have been calculated by the single frequency concentration variation method of Gopala Krishna are reported in **Table 1-4.**

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

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

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

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

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

The values of ε′ and ε′′ for the binary mixture 2,3-DCA+2-BE in the solution have been calculated using the short-circuited waveguide method of Heston *et.al* [11]. 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 ±1% and ±3% respectively. The variation of ε′ and ε′′ with weight fraction of solute in benzene for all binary mixtures is found to be linear. This shows that there is no change in the nature of the rotating intermolecular entities in the benzene solution. This ensures the applicability of the P.Debye theory [14] and that of Gopala Krishna's method in the studied concentration range of the binary mixtures in the benzene solutions.

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Table 1: Values of dielectric constant (ε′) dielectric loss (ε′′) and relaxation time (τ) of different mole fraction of 2,3-DCA in (2,3-DCA+2-BE) binary mixture in benzene at 20^0C.

Mole Fraction	Weight Fraction (W)	ε′ (±0.5%)	ε′′ (± 1%)	T (P.Sec)
0	0.0577 0.0984 0.1407 0.1792	1.967 2.184 2.221 2.298	0.090 0.110 0.134 0.169	2.60
0.26462	0.0563 0.1067 0.1519 0.1928	2.214 2.788 2.444 2.467	0.091 0.125 0.150 0.172	3.70
0.51913	0.0603 0.1139 0.1616 0.2045	2.131 2.878 2.318 2.338	0.117 0.164 0.176 0.181	3.50
0.76407	0.0642 0.1207 0.1707 0.2154	1.173 2.347 2.420 2.455	0.097 0.128 0.152 0.180	3.30
1	0.0679 0.1272 0.1793 0.2257	1.888 2.184 2.221 2.298	0.072 0.119 0.136 0.154	2.04

Table 2: Values of dielectric constant (ε′) dielectric loss (ε′′) and relaxation time (τ) of different mole fraction of 2,3-DCA in (2,3-DCA+2-BE) binary mixture in benzene at 30^0C.

Mole Fraction	Weight Fraction (W)	ε′ (±0.5%)	ε′′ (± 1%)	T (P.Sec)
0	0.0577 0.0984 0.1407 0.1792	2.080 2.259 2.380 2.467	0.098 0.119 0.166 0.180	2.50
0.26462	0.0563 0.1067 0.1519 0.1928	1.970 2.278 2.290 2.359	0.061 0.121 0.144 0.156	4.70
0.51913	0.0603 0.1139 0.1616 0.2045	2.008 2.278 2.298 2.355	0.069 0.121 0.144 0.156	4.50
0.76407	0.0642 0.1207 0.1707 0.2154	2.138 2.411 2.455 2.524	0.086 0.133 0.145 0.179	3.65
1	0.0679 0.1272 0.1793 0.2257	2.008 2.184 2.298 2.359	0.088 0.120 0.148 0.163	3.20

Table 3: Values of dielectric constant (ε′) dielectric loss (ε″) and relaxation time (τ) of different mole fraction of 2,3-DCA in (2,3-DCA+2-BE) binary mixture in benzene at 40^0C

Mole Fraction	Weight Fraction (W)	ε′ (±0.5%)	ε″ (± 1%)	T (P.Sec)
0	0.0577 0.0984 0.1407 0.1792	2.120 2.121 2.299 2.435	0.087 0.103 0.130 0.148	1.90
0.26462	0.0563 0.1067 0.1519 0.1928	2.028 2.259 2.338 2.422	0.069 0.125 0.149 0.167	2.90
0.51913	0.0603 0.1139 0.1616 0.2045	2.064 2.166 2.422 2.444	0.066 0.094 0.141 0.159	2.85
0.76407	0.0642 0.1207 0.1707 0.2154	2.028 2.240 2.318 2.359	0.089 0.127 0.150 0.162	2.45
1	0.0679 0.1272 0.1793 0.2257	1.988 2.221 2.298 2.359	0.085 0.116 0.148 0.161	2.08

Table 4: Values of dielectric constant (ε′) dielectric loss (ε″) and relaxation time (τ) of different mole fraction of 2,3-DCA in (2,3-DCA+2-BE) binary mixture in benzene at 50^0C.

Mole Fraction	Weight Fraction (W)	ε′ (±0.5%)	ε″ (± 1%)	T (P.Sec)
0	0.0577 0.0984 0.1407 0.1792	1.990 2.173 2.307 2.478	0.072 0.093 0.102 0.138	1.40
0.26462	0.0563 0.1067 0.1519 0.1928	1.955 2.318 2.422 2.467	0.060 0.120 0.150 0.166	2.35
0.51913	0.0603 0.1139 0.1616 0.2045	2.032 2.318 2.444 2.467	0.079 0.122 0.160 0.162	2.09
0.76407	0.0642 0.1207 0.1707 0.2154	1.926 2.278 2.444 2.489	0.054 0.087 0.117 0.151	2.05
1	0.0679 0.1272 0.1793 0.2257	2.113 2.467 2.633 2.684	0.068 0.122 0.158 0.177	1.85

Table 1-4 represent the values of ε′, ε″ and τ of the binary mixture 2,3-DCA+ 2-BE in benzene solution at temperatures 20^0C, 30^0C, 40^0C and 50^0C for different mole fractions of 2,3-DCA in the binary mixture. Non-linear variation of relaxation time with the increase in the mole -fraction of 2,3-

DCA in the binary mixture 2,3-DCA+2-BE shows solute-solute and solute solvent intermolecular association at all temperatures 20 ^{0}C, 30 ^{0}C, 40 ^{0}C and 50 ^{0}C. The linear variation of the relaxation time from its value corresponding to one constituent with the mole-fraction variation in the whole concentration range may be taken as the absence of any solute-solute association in the mixture[15]. On the other hand, non-linear variation of the relaxation time with the mole-fraction is interpreted as the possible solute-solute intermolecular association in the binary mixture [16]. In the present study, the non-linear variation of the relaxation time τ is found to increases linearly from the pure value of relaxation time of 2-BE in benzene solution [17]. In binary mixture of 2,3-DCA+2-BE, with increases in the mole fraction of 2,3-DCA at 30% mol the relaxation time increases at all temperatures 20 ^{0}C, 30 ^{0}C, 40 ^{0}C and 50 ^{0}C as shown in **Table 1-4**. The value of τ in binary mixture increases with the increases in the increases in the concentration of 2,3-DCA in binary mixture up to 50% mol there are 2,3-DCA and 2-BE molecule nearly equal in ratio, so solute-solute intermolecular association is proposed. Further increases the mole fraction of 2,3-DCA in binary mixture, the concentration of 2,3-DCA increases and the relaxation time reaches to the pure value of 2,3-DCA in the benzene solution. In the present case, the non-linear variation of τ is shown in **Fig 1.**

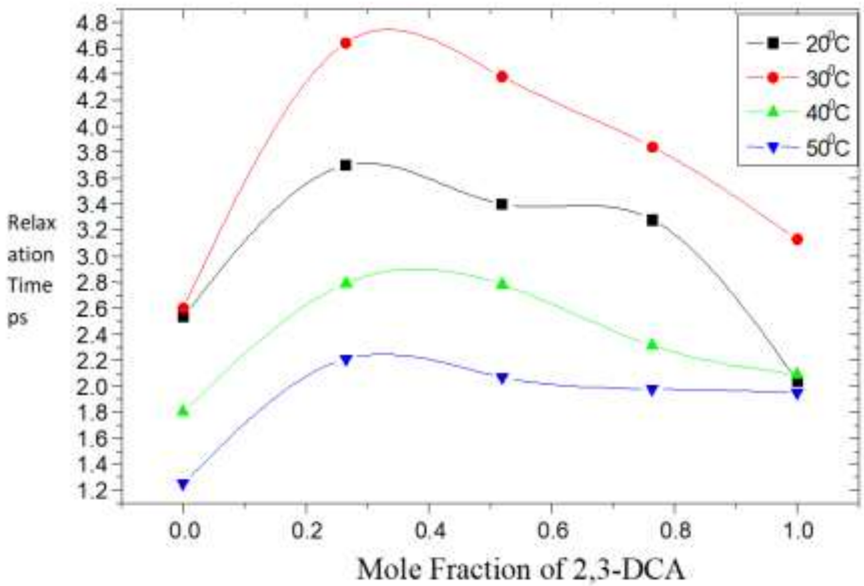

Figure 1: Relaxation time (τ) versus Mole fraction of 2,3-DCA in 2,3-DCA+2-BE mixture in benzene solution at different temperatures.

From **Fig 1** variation of the relaxation time (τ) first increases with the increase in mole fraction of 2,3-DCA in 2,3-DCA+2-BE binary mixture and attains a maximum value at mole fraction $X_{2,3\text{-DCA}}$=0.26462 of 2,3-DCA in the binary mixture. Then with further increase in the mole fraction of 2, 3-DCA in the binary mixture a sharp decrease in the relaxation time is observed and falls towards the value of pure 2,3-DCA in benzene solution. This behavior indicates solute-solute type of intermolecular association between 2, 3-DCA and 2-BE. This shows that intermolecular association is maximum at mole fraction $X_{2,\,3\text{-DCA}}$ = 0.26462 of 2, 3-DCA in 2, 3-DCA+2-BE binary mixture. Solute-solute type of intermolecular association is predicted in the whole concentration range in the binary mixture. For this concentration, the relaxation time of the intermolecular entities becomes longer than that of the individual molecules [18]. The intermolecular association between 2,3-DCA and 2-BE is maximum at a 30:70 mol % ratio and then deceases at higher mol% of 2,3-DCA in binary mixtures. In its whole concentration range, the relaxation time of 2,3-DCA+2-BE binary mixture remains longer that of pure 2,3-DCA. Therefore, the solute-solute type intermolecular association between 2, 3-DCA and 2-BE is indicated in its entire concentration range the intermolecular entity becomes much more voluminous than the individual molecule due to this association. The experiment was repeated a number of times so as to ensure the reproducibility of the above results. It is found that the above results are reproducible within the experimental accuracy range. It may be explain on the basis that the dielectric relaxation process involves the rotation of intermolecular entities.

CONCLUSION

The intermolecular association of 2,3-DCA+2-BE is maximum nearly at a 30:70 mol % ratio and then deceases at higher mol % of 2,3-DCA in binary mixtures. In its whole concentration range, the relaxation time of 2, 3-DCA+2-BE binary mixture remains longer than that of pure 2, 3-DCA. Therefore, the solute-solute type intermolecular association between 2, 3-DCA+2-BE is indicated in its entire concentration range. In view of above results, it is proposed that in the binary mixtures of 2,3-DCA+2-BE, 2,3-DCA exists in the oligomer structure resulting because of H-bonding and oligomer structure of 2,3-DCA interact with 2-BE molecules so as to give the maximum values of relaxation time at 30 mol % 2,3-DCA binary mixture.

Solute-solute intermolecular association can be interpreted because of the intermolecular association arising due to hydrogen bonding between 2,3-DCA+2-BE. In this hydrogen bonding $\delta+$ on hydrogen of hydroxyl group of 2-BE that form hydrogen bonding with nitrogen of 2,3-Dichloroaniline. Solute-Solvent intermolecular association can be interpreted because of the intermolecular association arising due fractional positive charge on hydrogen of 2-BE and lone pair of electron present on oxygen of benzene.

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