International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online)
An Open Access, Online International Journal Available at http://www.cibtech.org/jpms.htm
2014 Vol. 4 (2) April-June, pp. 13-18/Tumberphale et al.

Research Article

DIELECTRIC RELAXATION STUDIES OF BINARY MIXTURES OF ANILINE + 2-ETHOXYETHANOL IN BENZENE FROM MICROWAVE ABSORPTION DATA

U.B Tumberphale, R.S. Kawale, N.P. Pawar and *G.M. Kalamse
Microwave Research Laboratory, Department of Physics, Science College, Nanded- 431605, India
**Author for Correspondence*

ABSTRACT

The dielectric relaxation time (τ) and dipole moment (μ) for dilute solutions of binary mixtures of Aniline + 2-Ethoxy ethanol in Benzene are obtained at 9.85 GHz microwave frequency. Energy parameters (ΔH, ΔF, ΔS) for dielectric relaxation process have also been calculated. Comparison has been made with corresponding energy parameters for viscous flow. Debye's factor (C), Kalman's factor (C') and inverse relaxation time were computed. The variation of relaxation time and inverse relaxation time with mole fraction of Aniline in the mixture confirms solute – solute and solute – solvent interactions.

Keywords: *Dielectric Relaxation, Binary Mixture, Aniline, 2-Ethoxy Ethanol*

INTRODUCTION

The dielectric relaxation studies of binary mixture of polar molecules in non- polar solvent using microwave absorption method have been attempted by many researchers. Dielectric relaxation data obtained from microwave absorption studies may provide information regarding the presence of solute-solute and solute- solvent interactions. 2-Ethoxy ethanol (EE) is used widely as components of solvent in the commercial and industrial applications. It is very interesting class of solvent having the oxy (O) and hydroxyl (OH) group in the same molecule. Presence of both groups may form intra and inter molecular hydrogen bonds between O and OH groups of the same or different molecules (Kinart *et al.,* 2008).
Aniline having a phenyl group attached to an amino group having various applications in the field of medicine and dye industry. Taking in to consideration of the wide applications of EE and Aniline, we have undertaken the dielectric relaxation study.

MATERIALS AND METHOD

Pure samples of 2-Ethoxy ethanol (EE) and Aniline of AR grade were procured from M/S S.D. Fine Chemicals ltd Mumbai and Spectrochem. Pvt ltd. Mumbai, were used without further purification. The liquids were mixed according to their proportions by volume and kept for six hours in well stopper bottle to ensure good thermal equilibrium. X-band microwave bench was used to measure the wavelength of e.m. waves in the waveguide filled with dielectric. The liquids were mixed according to their proportions by volume. A set of dilute solution of (Aniline+EE) in Benzene were prepared. The dielectric constant (έ) loss factor (ε″), at 9.85 GHz microwave frequency was computed by Serber's method for different temperatures. All measurements were carried out at 20, 30, 40 and 50°C in a dielectric cell by circulating (EG + water) liquid using the constant temperature bath supplied by Nevtech Engineering Ltd. Mumbai.
The details' regarding experimental part is given in our earlier paper (Tumberphale *et al.*, 2013).

RESULTS AND DISCUSSION

Table (1) indicates that values of dielectric constant (ε′) and dielectric loss (ε″) has the decreasing trend with increasing temperature. This shows that the internal fields of the mixtures are not different from those of pure components (Rangra *et al.*, 2004; Kalaivani *et al.*, 2009; Kumar *et al.*, 2010), the values of relaxation time (τ) first increases with the increase in mole fraction of Aniline and then its value decreases and fall towards the pure Aniline. The non-linear variation of relaxation time (τ) shows the presence of solute-solute molecular association and it is maximum at X = 0.5 mole fraction of Aniline. The molecular association arising may be due to the interaction of the fractional positive charge on the hydrogen atom of (EE) and fractional negative charge on the nitrogen atom of Aniline.

Table 1: The values of dielectric constant (ε′), dielectric loss (ε″) and relaxation time (τ) for different weight fraction of solute of E.E., Aniline and their binary mixtures in Benzene at different temperatures

Temperatures			**293° K**			**303° K**			**313° K**			**323° K**	
Solute %	**Wt. fraction of solute**	**έ**	**ε″**	***τ ps***	**έ**	**ε″**	***τ ps***	**έ**	**ε″**	***τ ps***	**έ**	**ε″**	***τ ps***
	0.0583	2.664	0.166		2.637	0.144		2.611	0.130		2.598	0.113	
2-EE	0.1170	2.719	0.252		2.705	0.235		2.691	0.221		2.678	0.202	
100%	0.1658	2.946	0.355	5.884	2.930	0.341	5.835	2.914	0.325	5.803	2.898	0.302	5.706
	0.2095	3.124	0.416		3.114	0.398		3.099	0.380		3.082	0.351	
2-EE	0.0676	2.559	0.136		2.547	0.132		2.534	0.126		2.510	0.116	
(74%)	0.1267	2.719	0.258		2.705	0.252		2.678	0.242		2.650	0.229	
+	0.1787	2.898	0.351	6.337	2.883	0.344	6.304	2.867	0.335	6.223	2.836	0.319	6.126
Aniline	0.2248	3.117	0.436		3.082	0.417		3.064	0.405		3.030	0.383	
(26%)													
2-EE	0.0676	2.598	0.129		2.585	0.120		2.559	0.105		2.547	0.096	
(49%)	0.1267	2.852	0.268		2.836	0.246		2.821	0.225		2.777	0.194	
+	0.1787	2.946	0.338	7.129	2.930	0.321	7.016	2.914	0.295	6.660	2.883	0.270	6.460
Aniline	0.2249	3.082	0.398		3.047	0.373		3.030	0.348		3.013	0.327	
(51%)													
2-EE	0.0677	2.637	0.127		2.598	0.110		2.585	0.099		2.572	0.087	
(24%)	0.1268	2.748	0.200		2.719	0.175		2.691	0.155		2.664	0.138	
+	0.1788	2.898	0.282	6.353	2.883	0.260	6.078	2.867	0.238	5.83	2.836	0.214	5.787
Aniline	0.2250	3.135	0.388		3.117	0.365		3.099	0.340		3.082	0.322	
(76%)													
	0.0677	2.598	0.091		2.559	0.078		2.547	0.067		2.510	0.061	
Aniline	0.1269	2.806	0.195		2.762	0.167		2.748	0.146		2.733	0.128	
100%	0.1790	2.898	0.221	5.135	2.867	0.197	4.593	2.852	0.179	4.178	2.821	0.156	3.941
	0.2253	3.064	0.278		3.047	0.253		3.013	0.217		2.963	0.198	

Table (2) gives the dipole moment values, the temperature dependent of μ values of pure liquids and their binary mixtures may be due to the alignment of group dipoles (Sengwa *et al.*, 2006). The comparative study of $\mu_{exp.}$ and μ_{thero} values gives the information regarding the alignment of the dipoles of the constituent of polar binary mixture due to dipolar interaction.

According to Sengwa *et al.*, when $\mu_{exp.} = \mu_{thero}$, there is no change in the n*et al.*,ignment of the effective dipoles due to heterogeneous dipolar interaction. When $\mu_{exp.} > \mu_{thero}$ the heterogeneous dipolar interactions increases the number of parallel dipole alignment in the binary mixture and when $\mu_{exp.} < \mu_{thero}$ the heterogeneous dipolar interactions reduce the net number of parallel dipole alignment in the mixture. Applying these criteria to our case, $\mu_{exp.} > \mu_{thero}$ which indicates that the heterogeneous dipolar interactions increases the number of parallel dipole alignment in the binary mixture at all concentration and for different temperature also.

The variation of μ^2 with mole fraction of Aniline presented in Figure (3), the deviation from linearity may be attributed to the presence of solute-solute molecular association through hydrogen bonding (Rangra *et al.*, 2004, Gupta *et al.*, 2003). The maximum deviation from linearity is observed at X = 0.5 mole fraction of Aniline which supports to our earlier prediction from relaxation time (τ) curve. The dipole moment values increases with rise in temperature, which predicts the solute-solvent molecular association (Sharma *et al.*, 2008). The Debye factor (*C*) varies appreciably with temperature and the Kalman's Factor (*C′*) remains almost constant for all temperatures. This shows that Kalman's equation for dielectric relaxation time as function of viscosity is superior to the Debye's equation. The quantity η^x is the better representation of inner friction coefficient for dipole rotation as compared to microscopic viscosity (η).

Table 2: The values of Debye constant (C), Kalman's factor (C′) experimental values of dipole moment ($\mu_{exp.}$) and calculated values of dipole moment (μ_{cal})of E.E. + Aniline mixture in dilute solution of Benzene at different temperature

Solute %	Temp. ° K	*C x 10^{-8}*	*Ć x 10^{-8}*	*μ exp.D*	*μ cal.D*	*μ^2 exp.*	*μ^2 cal.*	*% deviation in μ^2*
2-EE	**293**	23.17	0.477	2.204	---	4.857	---	---
100%	**303**	27.20	0.503	2.255	---	5.086	---	---
	313	31.32	0.529	2.305	---	5.314	---	---
	323	34.13	0.545	2.357	---	5.554	---	---
2-EE (74%)	**293**	24.96	0.489	2.222	2.220	4.938	4.928	-0.20
+	**303**	29.39	0.517	2.274	2.271	5.170	5.158	-0.23
Aniline(26%)	**313**	33.58	0.539	2.324	2.321	5.402	5.389	-0.24
	323	36.64	0.555	2.376	2.373	5.646	5.633	-0.23
2-EE (49%)	**293**	28.07	0.373	2.244	2.235	5.037	4.997	-0.79
+	**303**	32.70	0.385	2.296	2.287	5.273	5.230	-0.81
Aniline(51%)	**313**	35.94	0.383	2.346	2.337	5.505	5.464	-0.74
	323	38.64	0.387	2.398	2.389	5.751	5.707	-0.76
2-EE (24%)	**293**	25.02	0.364	2.253	2.250	5.076	5.064	-0.23
+	**303**	28.33	0.367	2.305	2.302	5.312	5.300	-0.22
Aniline(76%)	**313**	31.46	0.369	2.355	2.353	5.548	5.536	-0.21
	323	34.61	0.382	2.408	2.404	5.799	5.780	-0.32
Aniline	**293**	20.22	1.928	2.265	---	5.130	---	---
100%	**303**	21.41	1.908	2.317	---	5.367	---	---
	313	22.54	1.902	2.368	---	5.607	---	---
	323	23.41	1.909	2.419	---	5.854	---	---

The experimental values and theoretical values of relaxation time (τ) presented in table (3) shows same trend, the bracketed values represent the percentage deviation. The percentage deviation is maximum at the mole fraction X = 0.51 of Aniline shows the occurrence of molecular association, which supports to our earlier conclusion. Fig (4) indicates the relaxation time (τ) calculated by various methods are plotted against mole fraction of aniline along with experimental values at 293^oK, it is clear that, values calculated from Yadav and Gandhi method are close to experimental values than other methods. Same conclusions are observed for 303^0K, 313^0K, 323^0K temperature.

The values of excess inverse relaxation time $\left(\frac{1}{\tau}\right)^e$ are calculated and presented in table (3). The excess inverse relaxation time values are found negative over entire range of mole fraction of Aniline. The negative deviation of excess inverse relaxation time in Figure (2) over entire range of mole fraction of Aniline suggests the solute-solvent interaction in such a way that, the binary mixture produces a field in which effective dipoles rotates slowly field will resist the rotation of the molecule this may be due to the strength of heterogeneous H-bond increases. Similar results are predicted by Sengwa *et al.*, (2004), Nimkar *et al.,* (2005). In the present case the maximum negative deviation of inverse relaxation time $\left(\frac{1}{\tau}\right)^e$ is also at X = 0.51 mole fraction of Aniline which supports to our earlier conclusion that the maximum molecular association exists at X = 0.51 mole fraction of Aniline.

The energy parameters of dielectric relaxation process and viscous flow process are presented in table (4), it is clear that $\Delta F_\tau < \Delta F_\eta$ this is in agreement with the fact that the process of viscous flow involved greater interference by the neighbours than does dielectric relaxation. Also ΔF_τ values increases with rise in temperature. This may be attributed to the decreasing viscosity of the medium with rise in temperature. It is also evident that the molar enthalpy of activation (ΔH_τ) values are less than the corresponding (ΔF_τ) values resulting in the negative molar entropy (ΔS_τ) of activation, indicating that the environment of the system is co-operative like that of the activated viscous flow state.(Rangra *et al.*,2004, Vimal Sharma *et al.*,2007, Raman Kumar *et al.*, 2010).

Table 3: Comparison of experimental values and computed values of relaxation time (τ) using different theoretical methods and excess inverse relaxation time $\left(\frac{1}{\tau}\right)^{e}$ for binary mixture of E.E. + Aniline at different temperature

Temp. ° K	Mole fraction of Aniline	*τ exp* *(p.s.)*	Theoretical values of *τ* calculated by S. M. Method	R. M. Method	Y. & G. Method	Madan's Method	Excess inverse relaxation time $\left(\frac{1}{\tau}\right)^{e}$
293	0.00	5.884	---	---	---	---	---
	0.26	6.337	5.688***(-11.40)***	5.669***(-11.78)***	5.698***(-11.21)***	5.659***(-11.98)***	-0.0186
	0.51	7.129	5.498***(-29.66)***	5.473***(-30.26)***	5.511***(-29.36)***	5.462***(-30.52)***	-0.0424
	0.76	6.353	5.314***(-19.55)***	5.297***(-19.93)***	5.324***(-19.38)***	5.288***(-20.13)***	-0.0314
	1.00	5.135	---	---	---	---	---
303	0.00	5.835	---	---	---	---	---
	0.26	6.304	5.510***(-14.41)***	5.450***(-15.67)***	5.537***(-13.85)***	5.435***(-15.98)***	-0.0249
	0.51	7.016	5.196***(-35.03)***	5.130***(-36.76)***	5.233***(-34.07***)	5.107***(-37.38)***	-0.0527
	0.76	6.078	4.890***(-24.29)***	4.840***(-25.58)***	5.134***(-18.39)***	4.829***(-25.86)***	-0.0421
	1.00	4.593	---	---	---	---	---
313	0.00	5.803	---	---	---	---	---
	0.26	6.223	5.378***(-15.71)***	5.269***(-18.11)***	5.426***(-14.69)***	5.236***(-18.85)***	-0.0291
	0.51	6.660	4.966***(-34.11)***	4.836***(-27.39***)	5.032***(-32.35)***	4.815***(-27.40)***	-0.0567
	0.76	5.830	4.566***(-27.68)***	4.478***(-30.19)***	4.619***(-26.22)***	4.464***(-30.60)***	-0.0518
	1.00	4.178	---	---	---	---	---
323	0.00	5.706	---	---	---	---	---
	0.26	6.126	5.245***(-16.80)***	5.110***(-16.58)***	5.302***(-15.54)***	5.087***(-20.42)***	-0.0325
	0.51	6.460	4.797***(-34.66)***	4.638***(-28.20)***	4.878***(-32.43)***	4.615***(-28.56)***	-0.0621
	0.76	5.787	4.366***(-32.55)***	4.257***(-35.94)***	4.428***(-30.69)***	4.243***(-36.39)***	-0.0608
	1.00	3.941	---	---	---	---	---

**(bracket terms indicates % deviation)*

Table 4: 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_{η}) for E.E. + Aniline and their binary mixtures in Benzene at different temperatures

Solute %	Temp. ° K	ΔF_{τ} *Kcal/mole*	ΔH_{τ} *Kcal/mole*	ΔS_{τ} *Kcal/mole*	ΔF_{η} *Kcal/mole*	ΔH_{η} *Kcal/mole*	ΔS_{η} *cal/mole*
2-EE 100%	**293**	2.085	**0.4183**	-5.689	2.976	**2.0153**	-3.279
	303	2.172		-5.786	3.003		-3.262
	313	2.260		-5.884	3.039		-3.271
	323	2.342		-6.095	3.098		-3.354
2-EE (74%) + Aniline(26%)	**293**	2.129	**0.3984**	-5.905	2.976	**2.0153**	-3.279
	303	2.218		-6.006	3.003		-3.262
	313	2.304		-6.086	3.039		-3.271
	323	2.387		-6.157	3.098		-3.354
2-EE (49%) + Aniline(51%)	**293**	2.197	**0.2382**	-6.686	2.976	**2.0153**	-3.279
	303	2.283		-6.747	3.003		-3.262
	313	2.346		-6.733	3.039		-3.271
	323	2.421		-6.758	3.098		-3.354
2-EE (24%) + Aniline(76%)	**293**	2.130	**0.2759**	-6.328	2.976	**2.0153**	-3.279
	303	2.196		-6.337	3.003		-3.262
	313	2.263		-6.348	3.039		-3.271
	323	2.351		-6.423	3.098		-3.354
Aniline 100%	**293**	2.006	**1.0479**	-3.270	2.976	**2.0153**	-3.279
	303	2.027		-3.232	3.003		-3.262
	313	2.055		-3.219	3.039		-3.271
	323	2.104		-3.269	3.098		-3.354

Research Article

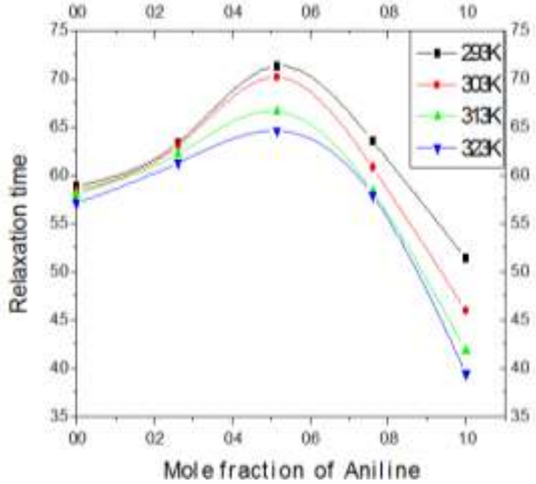

Figure 1 : Variation of Relaxation time V/s Mole Fraction of Aniline

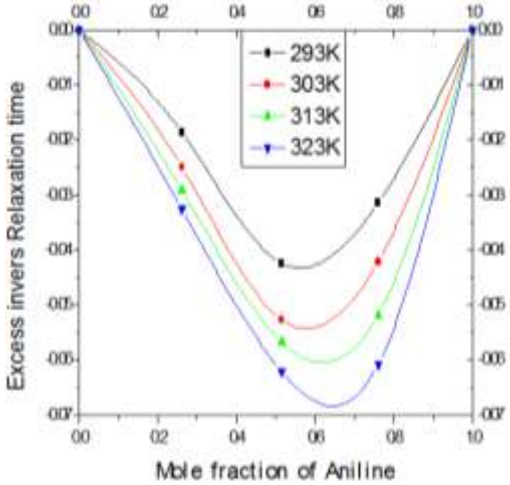

Figure 2 : Variation of $(1/\tau)^e$ V/s Mole Fraction of Aniline

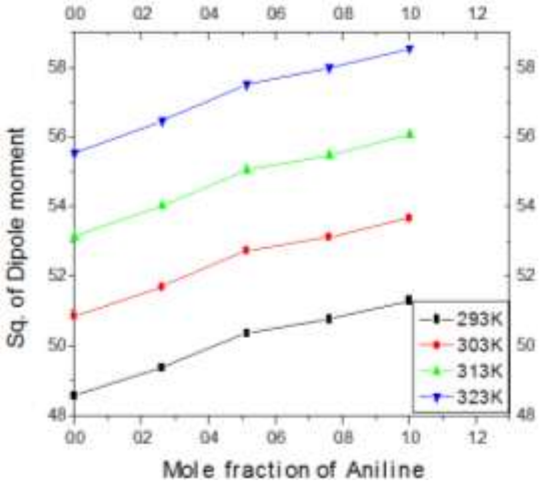

Figure 3 : Variation of μ^2 V/s Mole Fraction of Aniline

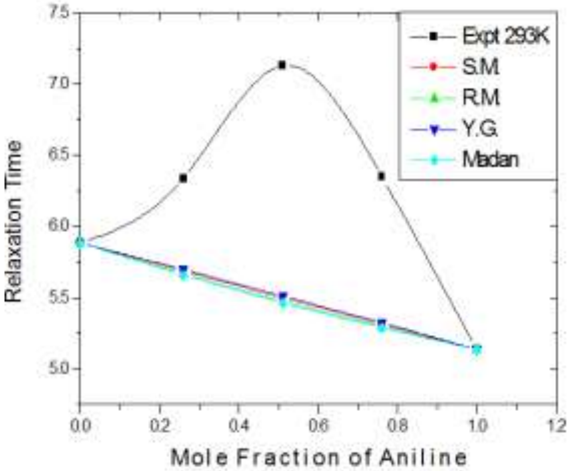

Figure 4: Variation of Relaxation time with Mole fraction of Aniline for Experimental and theoretical methods

REFERENCES

Gupta KK, Bansal AK, Singh PJ and Sharma KS (2003). Temperature dependence of dielectric relaxation of rigid polar molecules acetophenone, pyridine and their mixtures in dilute solutions of benzene. *Indian Journal of Pure and Applied Physics* **41** 57-63.

Kalaivani T and Krishnan S (2009). Dielectric relaxation studies of ternary liquid mixtures of aniline and substituted anilines with acrylonitrile in microwave region. *Indian Journal of Pure and Applied Physics* **47** 383-385

Kinart CM, Maj M, Cwiklinska A and Kinart WJ (2008). Densities, viscosities and relative permittivities of some n- alkoxyethanols with sulfolane at T= 303.15 K. *Journal of Molecular Liquids* **139** 1-7.

Nimkar MJ, Rekha Pande and Kalamse GM (2005). Dielectric Relaxation of Binary Mixtures of Diethylene Triamine + 2-Ethoxy ethanol in 1,4-Dioxane from Microwave Absorption Studies. *Asian Journal of Chemistry* **17**(1) 335-341.

Raman Kumar, Vinod Sharma and Rangra VS (2010). Dielectric relaxation studies of binary mixtures of tetrahydrofuran and N-methylacetamide in benzene solution using microwave absorption data. *Indian Journal of Pure and Applied Physics* **48** 415-419.

Rangra Virsing and Sharma DR (2004). Dielectric relaxation studies of binary mixtures of acetone and N-methylacetamide in benzene solution using microwave absorption data. *Indian Journal of Pure and Applied Physics* **42** 921-925.

Sengwa RJ, Madhvi and Abhilasha (2004). Solvent Effect on Dielectric Behaviour of Binary Mixtures of Mono Methyl Ether of Ethylene Glycol-Ethyl Alcohol. *Microwave and Optoelectronics* (Anamaya Pub., New Delhi) 104-109.

Sengwa RJ, Madhvi, Abhilasha and Sonu Sankhla (2006). Study of dielectric relaxation and dipole moment of some hydrogen bonded solvent binary mixtures in 1,4-dioxane. *Indian Journal of Pure and Applied Physics* **44** 943-952.

Tumberphale UB, Kalamse VG, Narwade BS and Kalamse GM (2013). Dielectric relaxation studies of binary mixtures of aniline + 2-methoxyethanol in benzene solution using microwave absorption data. *Bionano Frontier* **6**(1) 144-148

Vimal Sharma, Nagesh Thakur, Sharma DR, Negi NS and Rangra VS (2007). Dielectric relaxation study of binary mixtures of ethyl alcohol and N, N-dimethylformamide in benzene solution using microwave absorption data. *Indian Journal of Pure and Applied Physics* **45** 163-167.