DIELECTRIC PROPERTIES OF ALLYL AMINE AND 2- ETHOXY ETHANOL USING MICROWAVE FREQUENCY 9.85GHz AT ROOM TEMPERATURE

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ABSTRACT

Surber's technique is employed to measuredielectric constant (ε')of Allyl amine (AA)+2-ethoxyethanol (2-EE) for different mole fractions of Allyl amine (AA) at single microwave frequency 9.85 GHz using X-band microwave bench at room temperature 303 K. Density, viscosity and refractive index of AA+2-EE are also measured. Dielectric parameter, (ε') have been used to evaluate these derived dielectric parameters. The derived dielectric parameters, molar polarization (P_{12}), dielectric loss (ε") and loss tangent (tan δ) explicate the formation of complexes within the system. It is found that dielectric constant (ε'), dielectric loss (ε"), loss tangent (tan δ) varies non-linearly however molar polarization (P_{12}) activation energy (Ea),viscosity (η), and density (ρ) exponentially decreases with increasing mole fraction in binary mixture of Allyl amine (AA)+2-ethoxyethanol (2-EE). Data provide information regarding solute-solvent interaction in liquids with wobbling nature.

Keywords: Allyl amine, 2-Ethoxyethanol, dielectric constant, dielectric loss, molar polarization, activation energy, Molecular interaction.

INTRODUCTION

Over the past few years, analysis of dielectric properties of binary liquid mixtures are capturing a frequent recognition as the heating characteristics of a selected material via microwave radiation are dependent on its dielectric properties. (Jin, Dai and Huang, 1999) The utilization of microwave heating for promoting organic chemical transformations has been widely accepted by scientists (Lead beater, 2004; Adam, 2003). In chemical industry, knowledge of the properties of binary liquid mixtures is crucial in designs involving chemical separations (Ribeiro, Santos and Paiva, 2013), heat transfer (Rathnam, Mohite and Kumar, 2010; Rana, Chaube and Gadani, 2011), mass transfer (Nallani and Jaana, 2008; Pal, Kumar and Maan, 2013) and fluid flow (Pal and Kumar, 2006). When a binary mixture is formed, dielectric parameters don't vary linearly and Excess parameters deviate from linearity. The dielectric properties of binary liquid mixtures are useful to understand the nature of bonding between the

liquids. It is considerably necessary to examine the dielectric behaviour of AA and 2-EE binary system at 30ºC temperature at 9.85 GHz.

The neutral (NH_2) or charged ($-NH_{3+}$) group which are basic building block of amines, found in many biological systems (Gugliucci, 2004; Casero and Marton, 2007; Moinard, Cynober and Bandt, 2005). The presence of NH_2 group in amine plays an effective role in the inter-molecular hydrogen bonding (Deshmukh, Ingole and Shinde, 2019). Allylamine is colourless liquid, an organic compound associated with a primary aliphatic amine group with the formula $C_3H_5NH_2$. Allylamine, referred as 3-aminopropylene or prop-2-en-1-amine, is classified as a monoalkylamine. It is an antifungal medicine used to make antibiotic, diuretic and sedative medicines (Pawar, Swami and Patil, 2014). V. P. Pawar reports dielectric relaxation studies of allylamine-1,2,6-hexanetriol using Time Domain Reflectometry technique.

2-Ethoxyethanol is a common solvent often used for varnish removers, printing inks, duplicating fluids and wood stains. Conjointly employed in surface coatings such as lacquers and paints. Like other glycol ethers, is employed in the semiconductor industry. 2-EE and its mixtures with other solutes have aroused much interest among scientists in the last decades (Pal and Kumar, 2004; Awasthi, 2012; Nemmaniwar and Ahmed, 2018). Having found wide applications of both of the compounds, we investigate their binary mixtures to have productive data and knowledge.

MATERIALS AND METHODS

2.1 Materials: 2-Ethoxyethanol (EE) and Allyl amine (AA) of A.R. grade is procured from E-Merck Pvt. Ltd Mumbai and Spectrochem Ltd., Mumbai used without further purification. The two polar liquids were mixed according to their molar proportions and kept for six hours in a well stopper bottles to ensure good thermal equilibrium.

2.2 Measurements: The densities of the pure solvents and binary mixtures were determined with a 10 mL capacity single stem capillary pyknometer at the room temperature of (303 ± 0.01) K. The pyknometer was calibrated with doubly distilled water at atmospheric pressure and at the room temperature. The accuracy of the density measurements was estimated to be $\pm 1 \times 10^{-5}$ g cm^{-3}.The viscosities of the binary mixture were measured with Oswald's viscometer by measuring time required to measure the water and solution with Digital stop

watch model W_3 (Vitronics,Pune)of least count 0.1sec. The refractive indices for sodium D-lines were measured by using Abbe's Refractometer, model No.AR-204 with accuracy up to the five places of decimal. The dielectric constant (ε′) and dielectric loss (ε″) were measured by using Surber's technique (Jogdand, 2019) of measuring reflection coefficient from air dielectric boundary of the liquid using X-Band Microwave Bench with Klystron power supply model no-MITKP503. All the measurements were carried out at 30 ^{0} C for various mole fraction of AA.

Table 1: Comparison of experimental density, viscosity, Refractive Index and Dielectric Constant of pure AA and 2-EE with literature values at 303K.

Compound		**Density(ρ) gm/cm^3**	**Viscosity (η) Cp**	**Refractive Index**	**Dielectric Constant ε̇**
Allyl amine	Experimental	0.761	0.413	1.4205	6.3026
	literature	-	-	-	-
2-Ethoxy Ethanol	Experimental	0.9264	1.6442	1.4064	7.4579
	literature	0.9212 [19]	1.655 [19]	-	-
		0.9212 [20]	1.6541[20]	-	-

Table2: Mole fraction of AA(X), Density(ρ), Viscosity(η), Dielectric Constant(ε̇), Dielectric Loss(ε̈), Loss Tangent(tanδ), Molar Polarization (P_{12}), Activation Energy(E_a) and Square of the Refractive Index(n^2_D) of AA+2-EE at 303K.

Mole fraction of AA X	**Density gm/cm^3**	**Viscosity cp**	**ε̇**	***n*^{2}*D*sq. refractive**
0	0.9264	1.6442	7.4579	1.978045
0.1563	0.9179	1.5253	6.4670	1.992219
0.3154	0.8967	1.4083	6.4611	2.029369
0.4377	0.8756	1.1336	6.8005	2.003555
0.5647	0.8545	0.7533	6.7100	2.003584
0.6837	0.8334	0.9633	6.7110	2.00925
0.7956	0.8123	0.6556	6.7974	2.012114

0.9008	0.7911	0.5144	6.5089	2.026409
1	0.7610	0.4130	6.3026	2.017849

RESULTS AND DISCUSSION

For 2-EE measured data at room temperature 303K and the literature values were compared and found to be in good agreement (Table-1). The values of Mole fraction of AA (X), Density(ρ),viscosity(η), Dielectric Constant(έ) and Square of the Refractive Index(n^2_D) of binary mixtures are listed in **Table 2** These measured data was then used to calculate the dielectric parameters *viz*. values Dielectric Loss(ε̋),Loss Tangent(tanδ), Molar Polarization (P_{12}), Activation Energy(E_a) are tabulated in **Table 3** and Excess dielectric parameters are reported in **Table 4**. The standard relations given in literature (Tumberphale, Kawale and Kalmase, 2013) are used to calculate these parameters. The individual graphs of measured and calculated parameters are used to infer the intermolecular interactions between solute and solvent.

Table 3: Derived Dielectric Parameters for AA and 2- EE

Mole fraction of AA X	**ε̋**	**tanδ**	**P12 cm^3/mole**	**Ea Kcal/Mole**
0	1.872	0.2510	66.425	3.4528
0.1563	1.4253	0.2204	59.763	3.4076
0.3154	1.3183	0.204	57.37	3.3595
0.4377	1.5231	0.2240	56.65	3.2289
0.5647	1.5015	0.2237	55.127	2.9827
0.6837	1.4445	0.2152	53.13	3.1308
0.7956	1.4756	0.2171	51.793	2.8991
0.9008	1.268	0.1948	49.404	2.753
1	1.3903	0.2205	47.913	2.6208

Table 4: Derived Excess Dielectric Parameters for AA and 2-EE

Mole fraction of AA X	Δέ	Δε̈	Δtanδ	ΔP12	ΔEa	$\Delta n^2 D$
0	0	0	0	0	0	0
0.1563	-0.8103	-0.3714	-0.0258	-3.7688	0.0848	0.0735
0.3154	-0.6324	-0.4018	-0.0374	-3.2163	0.1691	0.1524
0.4377	-0.1517	-0.1381	-0.0137	-1.6723	0.1402	0.0283
0.5647	-0.0955	-0.0985	-0.0101	-0.8443	-0.0003	0.0144
0.6837	0.0430	-0.0982	-0.0150	-0.6384	0.2468	-0.0491
0.7956	0.2587	-0.0132	-0.0096	0.0962	0.1082	-0.0090
0.9008	0.0920	-0.1701	-0.0287	-0.3454	0.0497	-0.0207
1	0	0	0	0	0	0

3.1 Dielectric Parameters

3.1.1 Density: Figure 1 illustrates variation of density of mixture with mole fraction of allyl Amine in 2-EE. Density, viscosity and square of the refractive index are used to study the associational behaviour of weakly interacting liquids by R. K. Shukla (Shukla *et al.*, 2012). Density decreased with increase in molar concentration (*X*) of AA which may be due to the weakening of solute-solvent interactions in higher percentage of AA and increase in volume of system as AA percentage increases Deosarkar *et al.*, in 2013 reported same for Ethanol +Water system**.** This decrease in the density of solution causes molecular dissociation increasing the volume of the mixture.

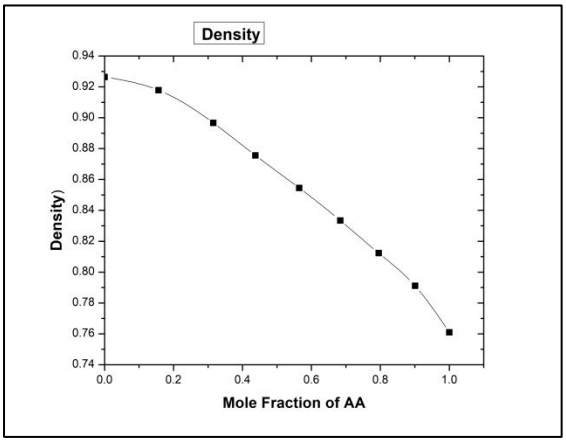

Figure1: Variation of density of mixture with Mole Fraction of AA in 2-EE.

3.1.2 Viscosity

Nonlinear reduction in the viscosity data exhibit that the molecules of system are held together by comparatively weaker intermolecular dipole-dipole interactions and the mixtures becomes less viscous. For present case the decrease in viscosity with increase in mole fraction of AA in 2-EE is illustrated **in Fig.2.**

The viscosity curve indicates formation of associates composed in this composition range is held together by comparatively stronger intermolecular dipole-dipole interactions at **X=0.6837.** As per P.G. Singh and K.S. Sharma (Singh and Sharma, 1996) Maxima in a viscosity curve may be associated with the formation of dissociated ions in the mixtures.

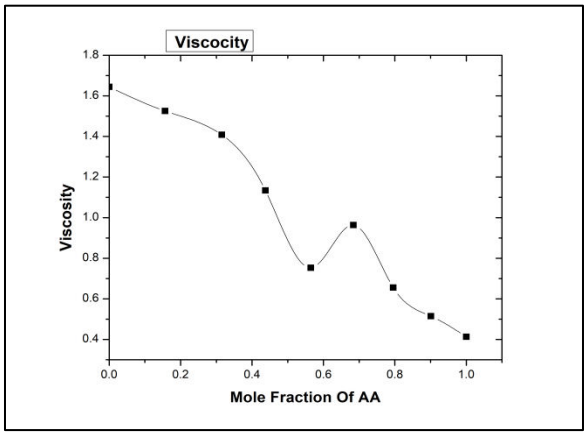

Figure 2: Variation of Viscosity of mixture with Mole Fraction of AA in 2-EE.

3.1.3 Refractive Index

According to **A.N. Sonar** (Sonar and Pawar, 2010) refractive index gives idea about geometrical structure and relative concentration of atom or molecule in a mixture. In our Investigation square of the refractive index **figure-3** exhibits some structural changes due to nonlinear increase in refractive index with mole fraction of AA.

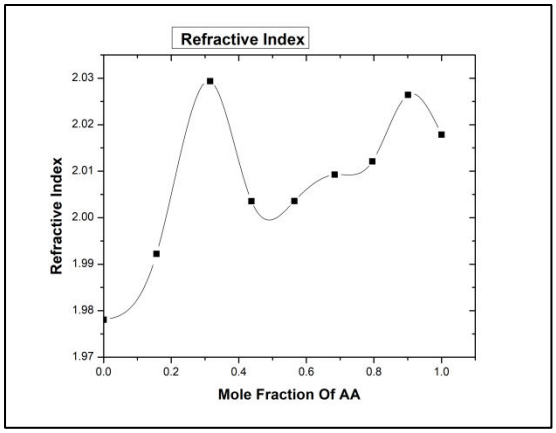

Figure 3: Variation of Refractive Index with Mole Fraction of AA in 2-EE.

3.1.4 Dielectric permittivity

The dielectric constant of liquid is a function of the number of molecules per cc, of the dipole moment, of the electronic and atomic polarization, of temperature and of the interaction of the molecules with each other (Kumler, 1935). In our investigation dielectric permittivity (ε') values gets decreases non-linearly showing maxima and minima as the concentration of AA increases depicted in **figure 4.** The relative permittivity of the mixtures is relatively high at **X=0.6837** where the number of molecules per cc, of the dipole moment slightly increases. The complex formation takes place at **X=0.6837** where change in the slope is maximum. Hence formation of 1:1 complex is present in the mixture.

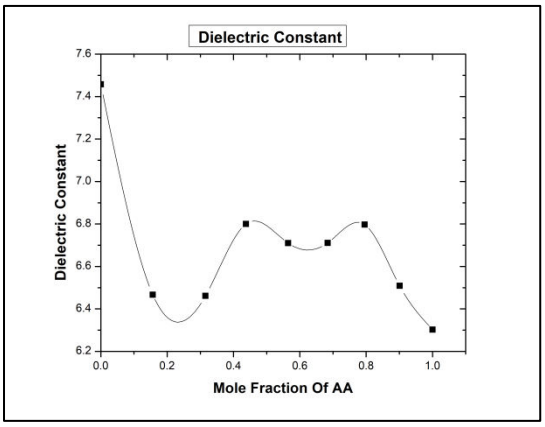

Figure 4: Variation of dielectric constant with Mole Fraction of AA in 2-EE.

3.1.5 Loss Tangent

Variation of tanδ with molar concentration of AA in the mixture shown in **figure 5** shows the absorption in the mixture varies nonlinearly with two maxima and minima. A pronounced

minimum between two maxima is observed at X=0.6837 in the variation of loss tangent with mole fraction of AA for binary system indicates the formation of complexes and are supported to our earlier conclusion regarding the formation of complexes. (Tumberphale, Kawale and Karle, 2012) (Nemmaniwar and Ahmed, 2018) U.Tumberphale et al and B.G. Nemmaniwar suggest that the formation of adduct complex at the minima.

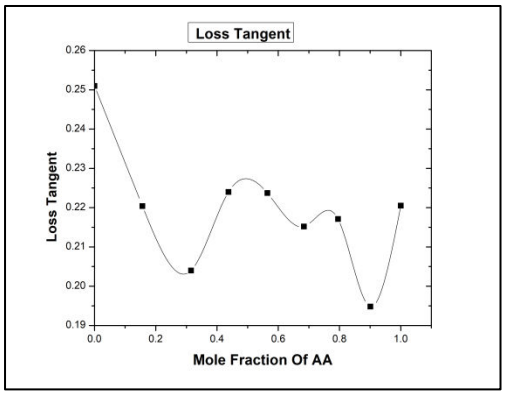

Figure 5: Variation of Loss Tangent with Mole Fraction of AA in 2-EE.

3.1.6 Molar polarization

Variation of Molar polarization (P_{12}), is depicted in **figure 6**. The interception of the straight lines represents two high and low regions of AA concentration is close to **X=0.6837** as a point of maximum concentration of the complex. Similar nature of P_{12}curve is obtained by Pande and Kalamse, 2005 for Alcohol-Amine system.

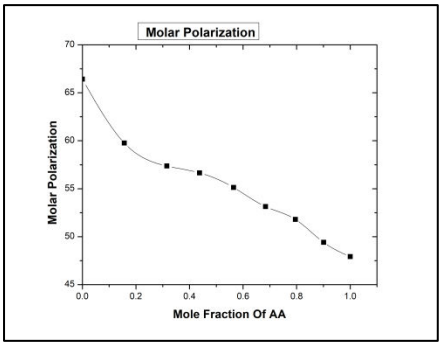

Figure 6: Variation of Molar Polarization with Mole Fraction of AA.

3.1.7 Activation energy

The nature of the reaction depends upon the activation energy. Fast reaction usually has a small Ea and those with a large Ea usually proceed slowly (Jogdand and Kadam, 2014). The graph of Activation energy (Ea) versus mole fraction (X) of AA is presented in **figure (7).** In the present system activation energy decreases non linearly with increasing mole fraction of Allyl amine in

the mixture except at X=0.6837 indicating reaction is fast at this mole fraction of AA and slower in rich region of solvent.

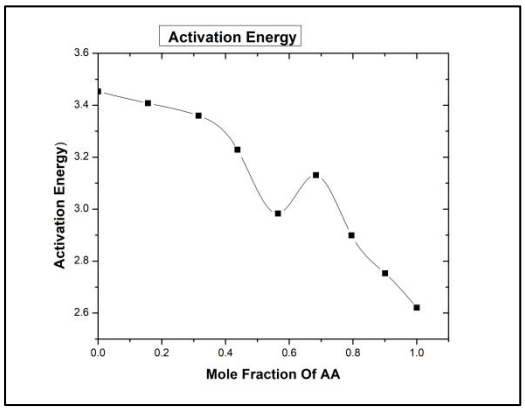

Figure-7. Variation of Activation Energy with Mole Fraction of AA in 2-EE

3.2 Excess dielectric parameters

3.2.1 Excess dielectric constant

In our study depicted in **Fig-8**, excess dielectric constant is negative for lower region of AA concentration and Positive for higher region of AA concentration. This negative value indicates that the molecules in the mixture form multimers through hydrogen bonding with reduction in effective dipole moment. This indicates the solute – solute interactions in such a way that total effective dipoles get reduced. Positive values of excess dielectric constant indicate increase in the effective number of parallel aligned dipoles in the same direction that contributing to the mixture dielectric polarization (Kamble, Sudake and Patil, 2011).

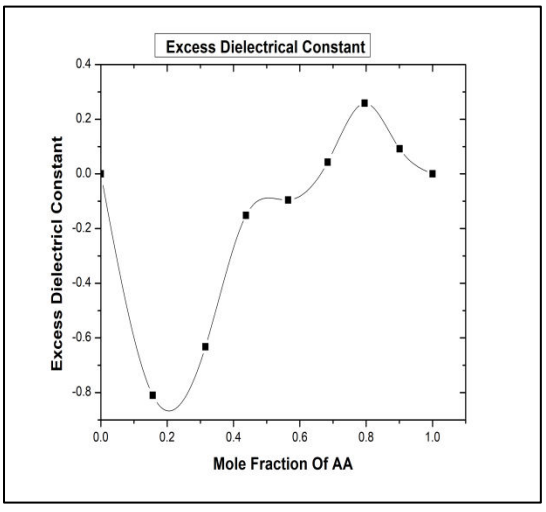

Figure 8: Variation of Excess Dielectric Constant with Mole Fraction of AA in 2-EE

3.2.2 Excess loss tangent

The excess loss with molar concentration of AA in **figure (9)** is associated with molecular motion which is governed by the complex forces of molecular interaction. In present case variation of excess loss tangent shows negative deviation over the entire range of mole fraction of AA with minima at X=0.6837

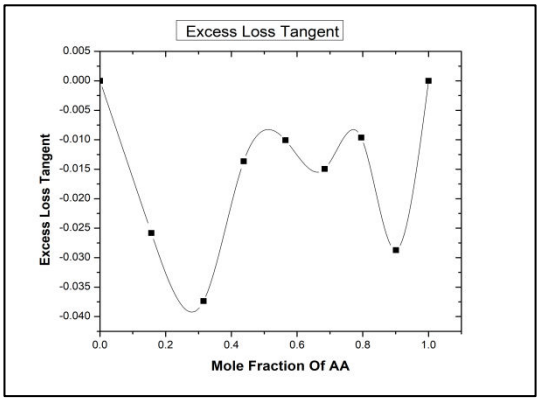

Figure 9: Variation of Excess Loss Tangent with Mole Fraction of AA in 2-EE

3.2.3 Excess molar polarization

Excess molar polarization **figure (10)** is the only relation that recognizes the short-range interaction between the dissimilar molecules and similar molecules in the mixtures taking molecular properties of the polar and non-polar liquids in the mixture into consideration. (Pandey and Gupta, 1983) Excess molar polarization remains negative for the rich region of 2-EE and positive for the rich region of AA. The present study shows the parallel alignment of molecular dipoles is the dominant factor with the short range interaction between the molecules.

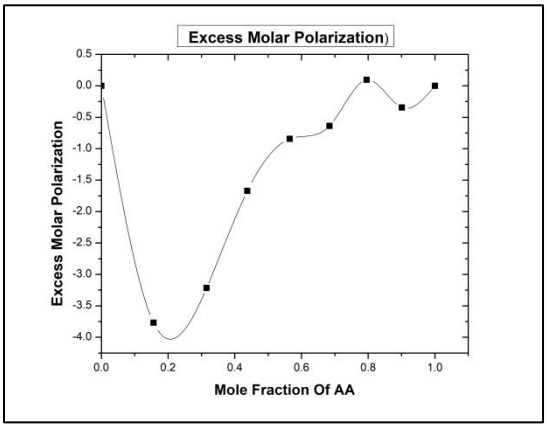

Figure 10: Variation of Excess Molar Polarization with Mole Fraction of AA

3.2.4 Excess activation energy

The deviation of excess activation energy depicted in **figure-11**is mostly positive indicates strong intersections between the AA and 2-EE molecules and the increase in the internal energy of the viscous flow. Positive value of excess activation energy supporting the presence of strong interactions in the system (Nemmaniwar, Jogdand and Kadam, 2013).

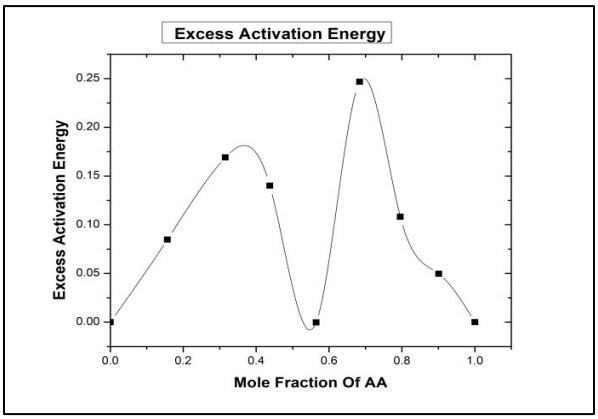

Figure 11: Variation of Excess Activation Energy with Mole Fraction of AA in 2-EE

3.2.5 Excess Viscosity

The excess viscosity gives an estimation of the intermolecular interaction. In present case as seen in figure -12the excess viscosity is positive for rich region of solvent and negative for rich region of solute. This indicates strong interaction in a very rich region of 2-EE and activation of dispersion forces in a solute AA. In the rich region of solvent 2-EE,As the molecular size increases, the magnitude of the excess viscosity increases (Moumouzias, Panopoulos and Ritzoulis, 1991). For negative deviation in rich region that the hydrogen bonds are broken and new species are formed. These new species consist of molecules having different geometrical configuration (Itzoulisgeoger).

CONCLUSIONS

The study of dielectric properties of Allyl amine (AA) and 2-Ethoxy Ethanol (2-EE), has been carried out to study solute - solvent interaction between the binary system at room temperature. The measured and calculated parameters were used to interpret the possible intermolecular interactions and the complex formation. The non-linear behaviour of dielectric constant versus

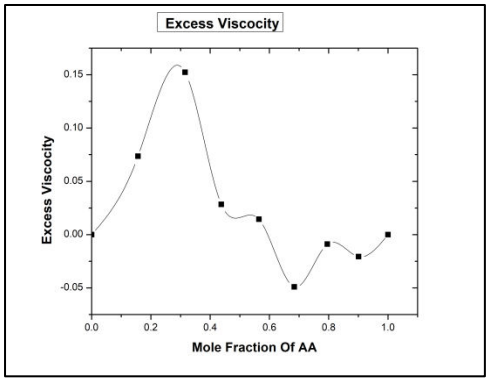

Figure 12: Variation of Excess Viscosity with Mole Fraction of AA in 2-EE

mole fraction of allyl amine suggests formation of complex in the mixture. The wobbling nature of the absorption curve may be due to a formation of Multicomplexes and polar-polar nature of binary mixture. The mixed negative and positive deviation for excess parameters in the mixture at room temperature indicates weak as well as strong solute-solvent molecular interaction through hydrogen bonding at rich region of solvent 2-EE and at rich region of solute AA respectively.

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