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Ultrasonic Study of Molecular Interaction in Binary Liquid Mixture Triethylamine in Benzene at 301.15K

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ABSTRACT

The Ultrasonic velocity, density, and viscosity have been measured for binary mixture of triethylamine (TEA) and benzene at four different temperatures for a constant frequency (5 MHz). These experimental data have been used to estimate the thermodynamic parameters such as ultrasonic velocity (u), viscosity (□), density (ρ), excess adiabatic compressibility (β_a^E), excess free length (L_f), excess free volume (V_f), excess viscosity (η^E), excess acoustic impedance (Z^E) for the solution. The excess values of the parameters are also evaluated and discussed.

Keywords: Ultrasonic velocity, Viscosity, Molecular interaction, Adiabatic compressibility, Acoustic impedance

INTRODUCTION

The studies of thermo-dynamical and transport properties of multi-component (binary and ternary) liquid mixtures and solutions have found wide application in chemical, textile, leather and nuclear industries. Ultrasonic investigations of liquid mixtures consisting of polar and non-polar components enable to understand the molecular interactions and structural behaviour of molecules and their mixtures [1-3]. The intermolecular interaction influences the structural arrangement along with the shape of the molecules.

For a better understanding of the physio-chemical properties and the molecular interaction between the participating components of these mixtures, ultrasonic velocities together with density and viscosity are measured at different temperatures for different concentration of the components in the mixture. These data furnish wealth of information about the interaction between ions, dipoles; hydrogen bonding, multi-polar and dispersive forces [4,5]. In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in terms of excess parameters rather than the actual values. The dispersion forces which are caused by correlated movements of the electrons in interacting molecules are responsible for positive excess values. Dipole-dipole, dipole-induced dipole, charge transfer interaction and hydrogen bonding between unlike molecules are responsible for possessing negative excess values [6-12].

MATERIALS AND METHODS

Experimental

The chemicals benzene and triethylamine used were of analytical grade and obtain from Merck chemicals private Ltd. (Purity 99.5%). The densities of pure components and binary mixtures were measured by psycnometer method with an accuracy 1 part in 10^4. Special attention was given to avoid the vaporization of solution [13-17]. Comparing their density with literature values checked the purity of chemicals. The mixtures of various concentrations in mole fraction were prepared. The ultrasonic velocities in pure liquids and their mixtures have been measured by ultrasonic interferometer supplied by Mittal Enterprises, New Delhi at a central frequency of 5 MHz with accuracy ± 0.01 m/s. The viscosity of pure and mixture is measured by an Ostwald's Viscometer with accuracy ± 0.001 $Nm^{-2}s$. The temperature of pure liquids and their mixtures is maintained constant with the help of constant temperature water bath with an accuracy of ± 0.01 K.

Theory

The adiabatic compressibility (β) has been calculated from sound velocity 'υ' and the density (ρ) of the medium using the relation

$$\beta = 1/\upsilon^2\rho \quad (1)$$

Intermolecular free length (L_f) has been determined by the equation.

$$L_f = K_T\sqrt{\beta} \quad (2)$$

Where K_T is a Jacobsen's constant.

The free volume L_f in terms of ultrasonic, velocity (υ) and the viscosity (η) of a liquid is

$$V_f = (M_{eff}\upsilon/K\eta)^{3/2} \quad (3)$$

Where M_{eff} is the effective molecular weight

$$M_{eff} = \Sigma m_i x \quad (4)$$

In which m_i and x_i are the molecular weights and mole fraction of individual constituents respectively and K is a temperature dependent constant equal to 4.28×10^9 for all liquids in MKS system.

Specific acoustic impedance (Z) is determined from equations,

$$Z = \upsilon.\rho \quad (5)$$

An excess value of ultrasonic related parameters has been calculated by using the relations.

$$\beta_a^E = (\beta_a)_{expt} - \sum X_i \beta_{ai} \quad (6)$$

$$V_f^E = (V_f)_{expt} - \sum X_i V_{fi} \quad (7)$$

$$L_f^E = (L_f)expt - \sum x_i (L_f)_i \quad (8)$$

Where V^E, β_a^E, Z^E and L_f^E are the excess values of molar volume, adiabatic compressibility, acoustic impedance and free length respectively.

RESULTS AND DISCUSSION

The benzene ring biologically active compound may replace by a triethylamine without loss of its activity. It is simplest aromatic compound containing sulphur atom and shows similar chemical properties as that of benzene. Ultrasonic velocity (υ), density (ρ), adiabatic compressibility (β) and other related excess thermodynamic parameters like excess adiabatic compressibility (β_a^E), excess acoustic impedance (Z^E), excess molar volume (V^E) and excess free length (L_f^E) are evaluated for binary mixture triethylamine in benzene over whole concentration at 301.15 K, 305.15 K, 309.15 K, 313.15 K and presented in **Tables 1-4** respectively [18-22].

In the binary liquid systems under investigation, the variation of ultrasonic velocity (υ), adiabatic compressibility (β_a^E), molar volume (V), free length (L_f) and acoustic impedance (Z) are shown in **Figures 1-5** respectively. Similarly **Figures 6-9** represents the variation in excess adiabatic compressibility (β_a^E), excess free volume (V_f^E), excess free length (L_f^E) and excess acoustic impedance (Z^E). These variations indicate the existence of molecular interaction between solvent and solute. The excess adiabatic compressibility (β_a^E) is positive over whole concentration range and it becomes minimum at a concentration (0.5) of triethylamine in benzene at observed temperatures. This indicates that the intermolecular interaction at this optimum at this concentration and it may leads to formation weak hydrogen bonded complex in binary liquid mixture. The same effects are also observed in excess free volume (V_f^E), excess excess free length (L_f^E) and excess acoustic impedance (Z^E). Beyond this optimum concentration, addition of solute (Benzene) in a solvent (Trethylamine) tries to break this weak complex structure and tends towards the values of pure components. It is evident that in the case of triethylamine, the normal inductive effect of methyl group has interaction with benzene is observed [23,24].

Table 1: Excess thermo-acoustic parameters for binary mixture containing TEA in benzene at 301.15 K

Mole Fraction(x)	U (ms^{-1})	$\eta\times10^{-3}$ ($Nm^{-2}s$)	$\rho\times10^{-3}$ (Kgm^{-3})	$\beta^E\times10^{-10}$ ($N^{-1}m^2$)	$L_f^E\times10^{-11}$ (m)	$V_f^E\times10^{-7}$ (m^3mole^{-1})	$\eta^E\times10^{-3}$ ($Nm^{-2}s$)	$Z^E\times10^5$ ($Kgm^{-2}s^{-1}$)
0.0	1372.5	0.6085	0.8416	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	1342.0	0.5421	0.8088	0.1365	0.0074	0.4986	-0.0421	-0.0367
0.2	1310.0	0.5132	0.8024	0.1123	0.0077	0.2213	-0.0468	-0.0381

0.3	1290.0	0.4755	0.7784	0.1490	0.0099	0.5828	-0.0602	-0.0522
0.4	1272.0	0.4455	0.7632	0.1060	0.0086	0.9409	-0.0660	-0.0527
0.5	1247.5	0.4293	0.7556	0.0908	0.0080	0.7001	-0.0579	-0.0479
0.6	1220.0	0.4213	0.7496	0.1286	0.0090	0.0094	-0.0416	-0.0430
0.7	1197.5	0.413	0.7456	0.0974	0.0071	-0.5646	-0.0257	-0.0318
0.8	1178.0	0.3987	0.7276	0.2275	0.0104	-0.6822	-0.0157	-0.0346
0.9	1165.0	0.3817	0.7216	0.1129	0.0052	-0.3642	-0.0085	-0.0182
1.0	1151.0	0.3659	0.7176	0.0000	0.0000	0.0000	0.0000	0.0000

Table 2: Excess thermo-acoustic parameters for binary mixture containing TEA in benzene at 305.15 K

Mole Fraction(x)	U (ms^{-1})	$\eta\times10^{-3}$ ($Nm^{-2}s$)	$\rho\times10^{-3}$ (Kgm^{-3})	$\beta^{E}\times10^{-10}$ ($N^{-1}m^{2}$)	$L_f^{E}\times10^{-11}$ (m)	$V_f^{E}\times10^{-7}$ (m^3mole^{-1})	$\eta^{E}\times10^{-3}$ ($Nm^{-2}s$)	$Z^{E}\times10^{5}$ ($Kgm^{-2}s^{-1}$)
0.0	1353.3	0.5500	0.8376	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	1323.3	0.4859	0.8048	0.1447	0.0076	0.8043	-0.0431	-0.0364
0.2	1291.0	0.4552	0.7984	0.1318	0.0084	0.7817	-0.0529	-0.0384
0.3	1272.0	0.4254	0.7744	0.1658	0.0104	1.1581	-0.0617	-0.0518
0.4	1246.6	0.4027	0.7592	0.2286	0.0130	1.2875	-0.0634	-0.0587
0.5	1228.0	0.3847	0.7516	0.1437	0.0099	1.4304	-0.0605	-0.0495
0.6	1200.0	0.3801	0.7456	0.2025	0.0115	0.5388	-0.0441	-0.0455
0.7	1178.5	0.3713	0.7416	0.1654	0.0094	0.0870	-0.0319	-0.0341
0.8	1152.8	0.3591	0.7236	0.4234	0.0167	-0.1692	-0.0231	-0.0416
0.9	1145.0	0.3492	0.7176	0.2216	0.0087	-0.0832	-0.0121	-0.0219
1.0	1137.0	0.3403	0.7136	0.0000	0.0000	0.0000	0.0000	0.0000

Table 3: Excess thermo-acoustic parameters for binary mixture containing TEA in benzene at 309.15 K

Mole Fraction(x)	U (ms^{-1})	$\eta\times10^{-3}$ ($Nm^{-2}s$)	$\rho\times10^{-3}$ (Kgm^{-3})	$\beta^{E}\times10^{-10}$ ($N^{-1}m^{2}$)	$L_f^{E}\times10^{-11}$ (m)	$V_f^{E}\times10^{-7}$ (m^3mole^{-1})	$\eta^{E}\times10^{-3}$ ($Nm^{-2}s$)	$Z^{E}\times10^{5}$ ($Kgm^{-2}s^{-1}$)
0.0	1332.8	0.4949	0.8336	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	1293.3	0.4530	0.8008	0.2848	0.0128	0.2555	-0.0248	-0.0446
0.2	1256.6	0.4267	0.7944	0.3630	0.0168	0.1103	-0.0338	-0.0511
0.3	1233.3	0.3984	0.7704	0.4971	0.0222	0.4959	-0.0449	-0.0684
0.4	1202.8	0.3785	0.7552	0.6881	0.0289	0.4705	-0.0477	-0.0794
0.5	1186.6	0.3622	0.7476	0.6075	0.0256	0.6452	-0.0469	-0.0698
0.6	1170.0	0.3584	0.7416	0.5302	0.0222	-0.0421	-0.0335	-0.0584
0.7	1157.5	0.3486	0.7376	0.3707	0.0160	-0.1280	-0.0261	-0.0414
0.8	1145.3	0.3373	0.7196	0.4182	0.0163	0.0152	-0.0202	-0.0403
0.9	1139.0	0.3297	0.7136	0.1980	0.0079	0.0697	-0.0107	-0.0208
1.0	1130.0	0.3232	0.7099	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4: Excess thermo-acoustic parameters for binary mixture containing TEA in benzene at 313.15 K

Mole Fraction(x)	U (ms^{-1})	$\eta\times10^{-3}$ ($Nm^{-2}s$)	$\rho\times10^{-3}$ (Kgm^{-3})	$\beta^{E}\times10^{-10}$ ($N^{-1}m^{2}$)	$L_f^{E}\times10^{-11}$ (m)	$V_f^{E}\times10^{-7}$ (m^3mole^{-1})	$\eta^{E}\times10^{-3}$ ($Nm^{-2}s$)	$Z^{E}\times10^{5}$ ($Kgm^{-2}s^{-1}$)
0.0	1302.5	0.4751	0.8296	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	1260.0	0.4370	0.7968	0.3654	0.0157	0.1041	-0.0218	-0.0474
0.2	1236.6	0.4136	0.7904	0.2993	0.0141	0.0437	-0.0289	-0.0443
0.3	1210.0	0.3846	0.7664	0.5031	0.0221	0.4504	-0.0416	-0.0648
0.4	1185.5	0.3668	0.7512	0.6285	0.0264	0.4329	-0.0431	-0.0720
0.5	1168.0	0.3525	0.7436	0.5796	0.0243	0.4504	-0.0411	-0.0644
0.6	1156.0	0.3459	0.7376	0.4326	0.0187	0.0783	-0.0313	-0.0507
0.7	1142.0	0.3369	0.7336	0.3050	0.0136	-0.0921	-0.0241	-0.0360
0.8	1129.0	0.3282	0.7156	0.3816	0.0150	-0.1949	-0.0164	-0.0362
0.9	1123.0	0.3196	0.7096	0.1581	0.0065	-0.0188	-0.0087	-0.0177
1.0	1112.5	0.3120	0.7056	0.0000	0.0000	0.0000	0.0000	0.0000

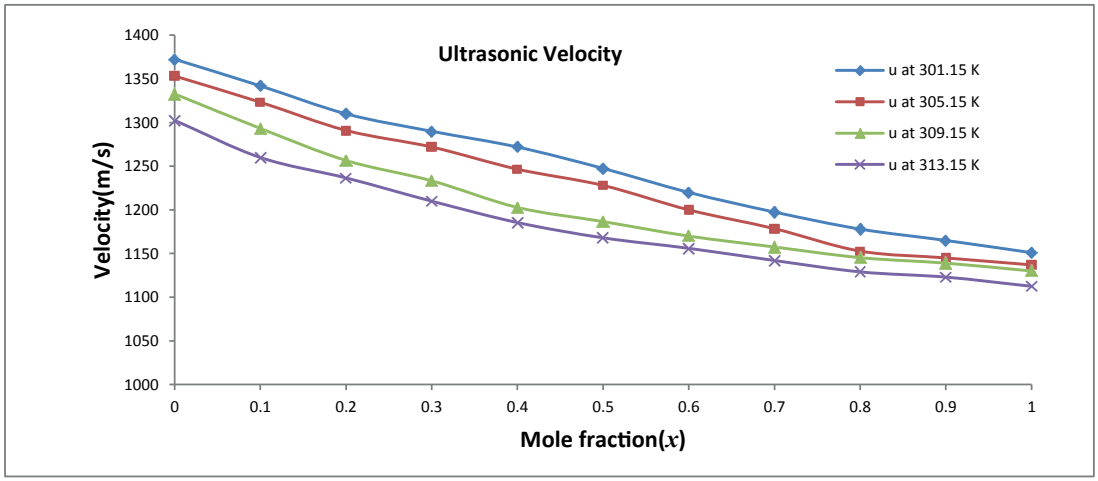

Figure 1: Variation of Ultrasonic velocity with mole fraction for binary liquid mixture containing Triethylamine in Benzene at 301.15 K, 305.15 K, 309.15 K, 313.15 K

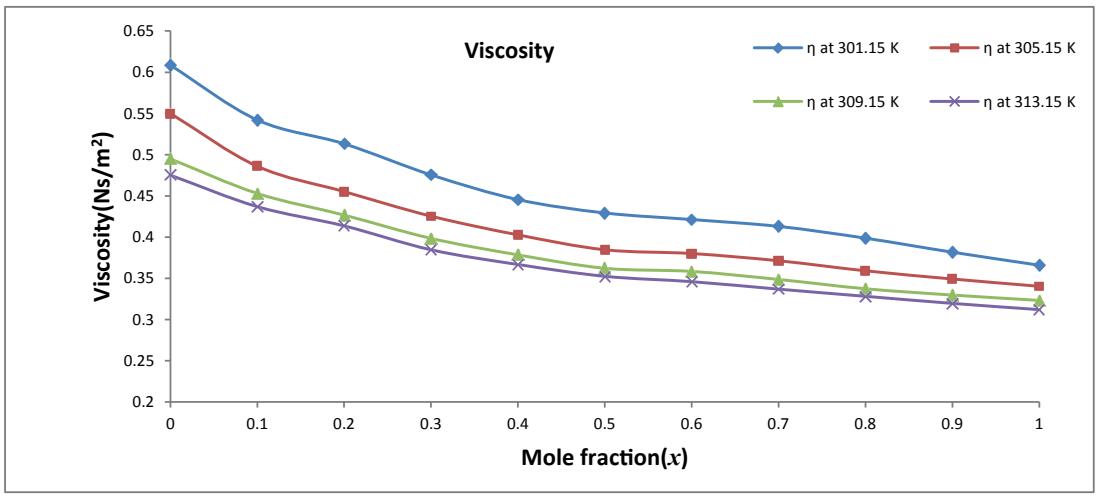

Figure 2: Variation of Viscosity with mole fraction for binary liquid mixture containing Triethylamine in Benzene at 301.15 K, 305.15 K, 309.15 K, 313.15 K

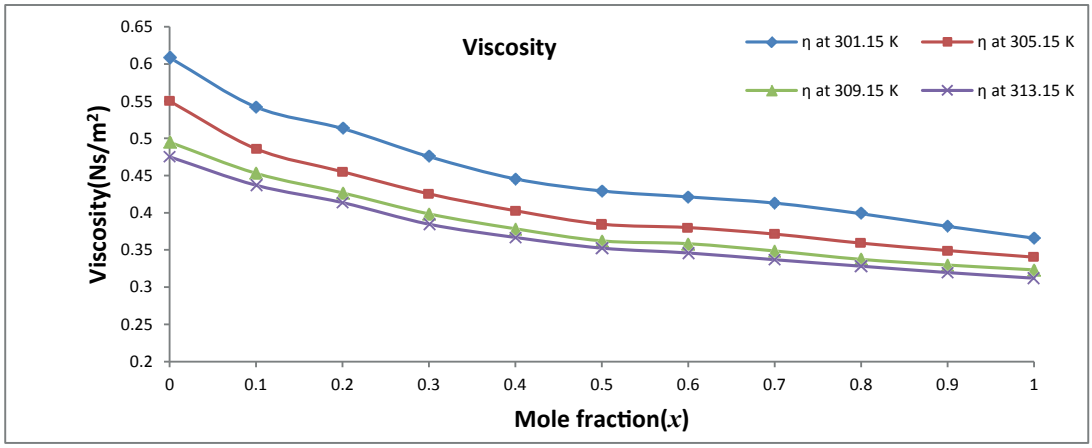

Figure 3: Variation of Density with mole fraction for binary liquid mixture containing Triethylamine in Benzene at 301.15 K, 305.15 K, 309.15 K, 313.15 K

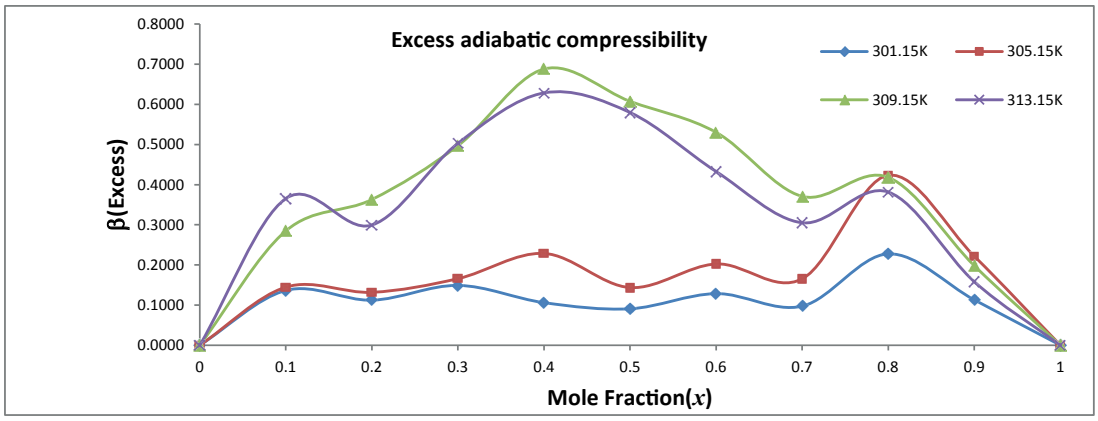

Figure 4: Variation of β (Excess) with mole fraction for binary liquid mixture containing Triethylamine in Benzene at 301.15 K, 305.15 K, 309.15 K, 313.15 K

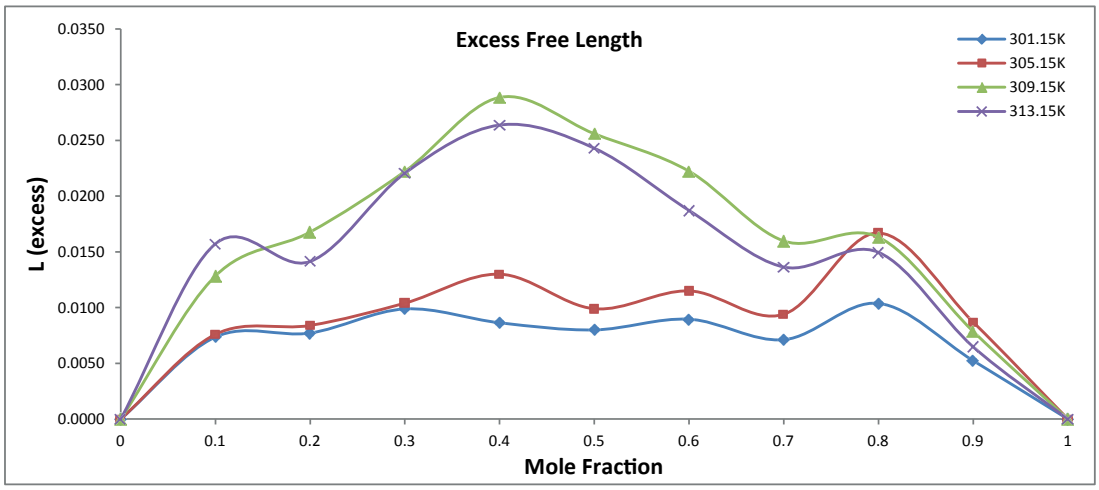

Figure 5: variation of L_f (Excess) with mole fraction for binary liquid mixture containing Triethylamine in Benzene at 301.15 K, 305.15 K, 309.15 K, 313.15 K

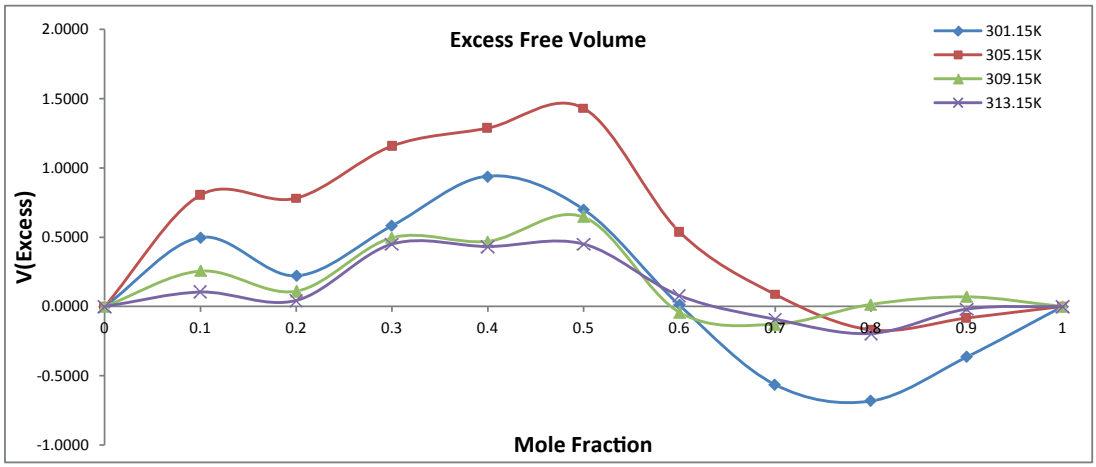

Figure 6: Variation of Excess free volume with mole fraction for binary liquid mixture containing Triethylamine in Benzene at 301.15 K, 305.15 K, 309.15 K, 313.15 K

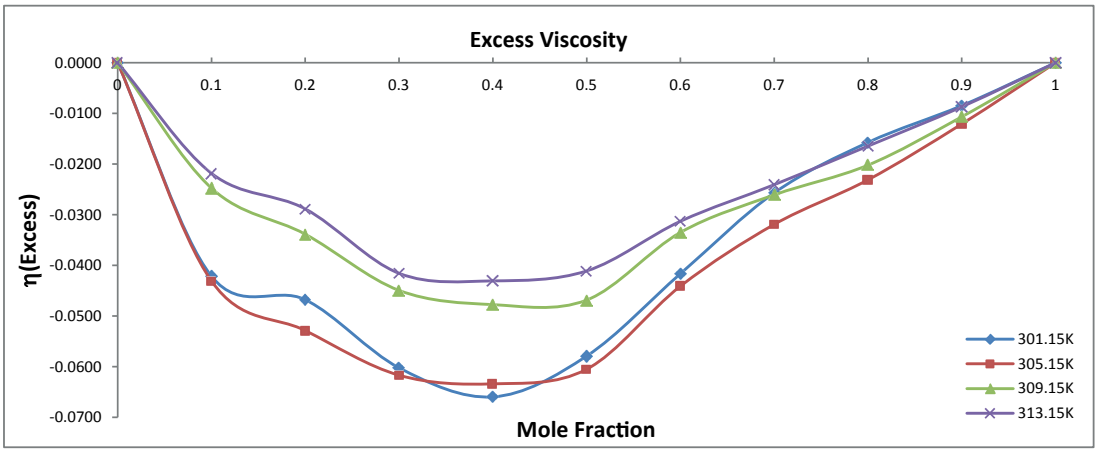

Figure 7: Variation of η (Excess) with mole fraction for binary liquid mixture containing Triethylamine in Benzene at 301.15 K, 305.15 K, 309.15 K, 313.15 K

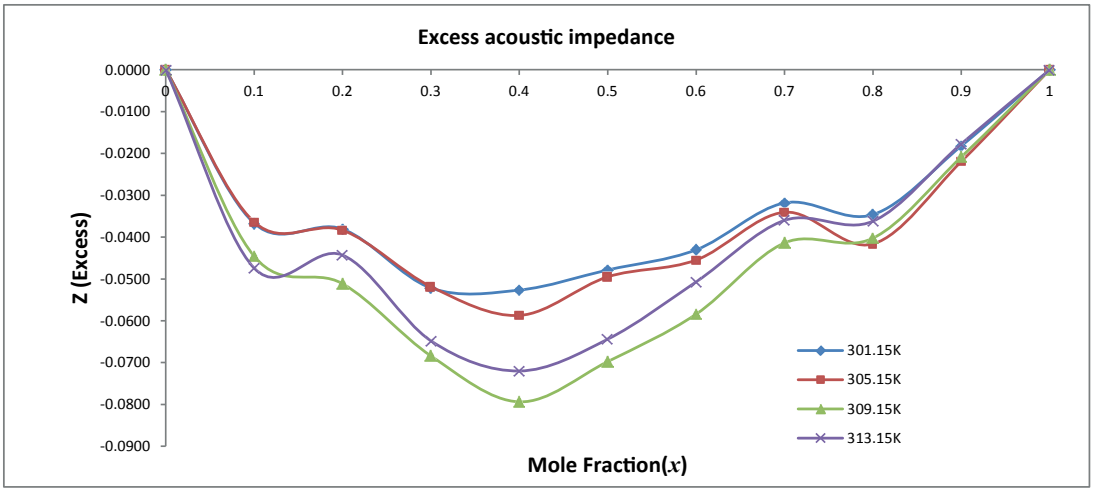

Figure 8: Variation of *Z* (Excess) with mole fraction for binary liquid mixture containing Triethylamine in Benzene at 301.15 K, 305.15 K, 309.15 K, 313.15 K

CONCLUSION

The acoustic data of Ultrasonic velocity (υ), density (ρ) and related thermodynamic parameters with their excess values of triethylmine in benzene and over the whole concentration range may suggest the existence of a strong intermolecular interaction. The negative values of some acoustic parameters like excess compressibility indicate a strong intermolecular interaction in the constitute molecules of binary liquid mixture triethylamine in benzene. The excess values of thermo-acoustic parameters of binary mixture triethylamine in benzene were positive over whole concentration. This positive contribution is from the rupture of hydrogen bond of triethylamine in benzene and dipole-induced dipole interaction.

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