

# Ultrasonic Study of Acoustical Parameters in Binary Liquid Mixture (Triethylamine With n-hexane) at 301.15K

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**Abstract:** The ultrasonic velocity ( $u$ ), density ( $\rho$ ) and viscosity ( $\eta$ ) have been measured in binary liquid mixtures containing triethylamine with n-hexane. From these data some of acoustical parameters such as adiabatic compressibility ( $\beta_{ad}$ ), free length ( $L_f$ ), free volume ( $V_f$ ), internal pressure ( $\pi_i$ ), molar volume ( $V_m$ ), relaxation time ( $\tau$ ), Gibb's free energy ( $\Delta G$ ), Rao's constant ( $R$ ), Wada's constant ( $W$ ), Enthalpy ( $E$ ), cohesive energy (CE) and molecular interaction parameter with respect to velocity ( $\chi_V$ ) have also been calculated. Have been computed using the standard relations. The excess values of these parameters are also evaluated over the whole concentration range. The present paper represents the nonlinear variation of ultrasonic and thermo-acoustical parameters lead to increased hydrogen bonding interaction between solute and solvent molecules. The result is interpreted in terms of molecular interaction such as dipole-dipole interaction through hydrogen bonding between components of mixtures. The dependence of excess properties of mixture compositions were compared and discuss in terms of the intermolecular free length and other factors affecting the solvation and self association effect. The excess values of these indicate dipole-induced dipole interaction complexity in the binary liquid mixture.

**Keywords:** binary liquid mixture, ultrasonic velocity, density, viscosity, adiabatic compressibility ( $\beta_{ad}$ ), free length ( $L_f$ ), free volume ( $V_f$ ), internal pressure ( $\pi_i$ ), molar volume ( $V_m$ ), relaxation time ( $\tau$ ), Gibb's free energy ( $\Delta G$ ), Rao's constant ( $R$ ), Wada's constant ( $W$ ), Enthalpy ( $E$ ), cohesive energy (CE)

## 1. Introduction

In recent years, the measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. The ultrasonic velocity measurements are highly sensitive to molecular interactions and can be used to provide qualitative information about the physical nature and strength of molecular interaction in the liquid mixtures [1-3]. Ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules and has been adequately employed in understanding the nature of molecular interaction in pure liquids [4-6]. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components [7- 8] as well as strongly interacting components.

The study of molecular association in organic binary mixtures having alkane as one of the components is of particular interest, since alkane are strongly self-associated liquid having a three dimensional network of hydrogen bond and can be associated with any other group having some degree of polar attractions. Accurate knowledge of thermodynamic mixing properties such as adiabatic compressibility, intermolecular free length, free volume, internal pressure and molar volume and their excess values for mixtures of protic, non-protic and associated liquids has a great importance in theoretical and applied areas of research.

Development in science and technology for non – destructive technique are spectacular and holds significant

possibilities for better new applications in molecular structure, molecular interactions, medicines and underwater acoustics. Development of sensors, electronic instrumentation and computer software added sophistication to the experimental and theoretical agreement of different ultrasonic parameters [9-12]. Thermodynamics studies of binary liquid mixtures have attracted much attention of scientists. These physico-chemical analyses are used to handle the mixtures of hydrocarbons, alcohols, aldehydes, ketones etc. The measurement of ultrasonic speed enables us to the accurate measurement of some useful acoustic and thermodynamic parameters and their excess values [13-18]. These excess values of ultrasonic velocity, adiabatic compressibility, molar volume and viscosity in binary liquid mixture are useful in understanding the solute-solvent interactions. The study of molecular association in binary liquid mixture having alcohol as one of component is of particular interest since alcohols are strongly self associated liquids having three dimensional network of hydrogen bonding and can be associate with any other group having some degree of polar attraction[19-21]. The variation in ultrasonic velocity gives information about the bonding between molecules and formation of complexes at various concentration and temperature through molecular interactions[22-24].

## 2. Experimental

The chemicals triethylamine and n-hexane 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 hydrostatic sinker method with an accuracy 1 part in  $10^{+5}$ . Special attention was

given to avoid the vaporization of solution. 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  $\pm 0.01$  m/s. The viscosity of pure and mixture is measured by an Ostwald/s Viscometer with accuracy  $\pm 0.001 \text{ Nm}^{-2}\text{s}$ . The temperature of pure liquids and their mixtures is maintained constant temperature water bath with an accuracy of  $\pm 0.01\text{K}$ .

### 3. Theoretical Aspect

The adiabatic compressibility ( $\beta$ ) has been calculated from sound velocity 'u' and the density ( $\rho$ ) of the medium using the relation

$$\beta = \frac{1}{u^2 \rho} \quad (1)$$

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 ( $V_f$ ) in terms of ultrasonic, velocity (u) and the viscosity ( $\eta$ ) of a liquid is

$$V_f = \left( \frac{M_{eff} u}{\eta} \right)^{3/2} \quad (3)$$

Where  $M_{eff}$  is the effective molecular weight

$$M_{eff} = \sum m_i x_i \quad (4)$$

In which  $m_i$  &  $x_i$  are the molecular weights and mole fraction of individual constituents respectively and K is a

temperature dependent constant equal to  $4.28 \times 10^9$  for all liquids in MKS system.

The specific acoustic impedance is given by,

$$Z = U \rho \quad (5)$$

Where 'U' is the velocity and ' $\rho$ ' is the density of the mixture.

Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and impurities. The relaxation time can be calculated from the relation,

$$\tau = 4/3. (\beta \eta) \quad (6)$$

Where ' $\beta$ ' is the adiabatic compressibility and ' $\eta$ ' is the viscosity of the mixture.

The molar sound velocity (R) was calculated by the equation

$$R = (M_{eff} / \rho) U^{1/3} \quad (7)$$

Where U is the ultrasonic velocity of the mixture.

The molar compressibility or Wada's constant (W), was calculated by the equation

$$W = (M / \rho) \beta^{-1/7} \quad (8)$$

Where M is the relative molar mass and  $\beta$  is the adiabatic compressibility.

The enthalpy of binary liquid mixture is given by

$$H = \Pi V_m \quad (9)$$

where  $V_m$  is the molar volume.

### 4. Results and Discussion

Ultrasonic velocity (u), density ( $\rho$ ), viscosity ( $\eta$ ) and other related thermodynamic parameters are evaluated for binary mixture triethylamine (TEA) in n-hexane over whole concentration at 301.15 K, 305.15 K, 309.15K and 313.15K.

**Table 1:** For binary liquid mixture containing Triethylamine in n-hexane at 301.15K.

Mole Fraction (x)	U (ms <sup>-1</sup> )	$\rho \times 10^{-3}$ (Kg m <sup>-3</sup> )	$V_m \times 10^3$ (m <sup>3</sup> mole <sup>-1</sup> )	$\tau \times 10^{-14}$ (s)	R	W	$H \times 10^7$ KJ mole <sup>-1</sup>
0.0	940.0	0.6513	132.32	0.8013	12026.74	3.8411	2.4162
0.1	956.7	0.6571	133.43	0.7749	12679.48	3.849	2.4114
0.2	968.3	0.6655	134	0.7552	13203.95	3.8452	2.4184
0.3	989.5	0.6721	134.92	0.737	13683.2	3.8422	2.4326
0.4	1001.2	0.6788	135.8	0.7234	14126.93	3.8489	2.4455
0.5	1010.1	0.684	136.96	0.7207	14317.66	3.8676	2.4633
0.6	1032.3	0.6919	137.57	0.6866	15342.28	3.8549	2.4687
0.7	1049.7	0.6966	138.79	0.6642	16196.87	3.8664	2.4564
0.8	1060.0	0.7051	139.25	0.6466	16852.73	3.8615	2.4805
0.9	1076.3	0.7105	140.3	0.6464	16931.64	3.8696	2.4987
1.0	1110.0	0.718	140.93	0.6171	18001.43	3.8473	2.5509

**Table-2:** For binary liquid mixture containing Triethylamine in n-hexane at 305.15K.

Mole Fraction(x)	U (ms <sup>-1</sup> )	$\rho \times 10^{-3}$ (Kg m <sup>-3</sup> )	$V_m$ (m <sup>3</sup> )	$\tau \times 10^{-14}$ (s)	R	W	$H \times 10^7$ KJ mole <sup>-1</sup>
0.0	931.3	0.6473	133.13	0.7467	13566.13	3.8784	2.3346
0.1	943.2	0.6497	134.99	0.7274	14286.93	3.9162	2.3219
0.2	951.3	0.6577	135.59	0.7144	14742.11	3.9173	2.3317
0.3	965.2	0.6634	136.69	0.7048	15116.19	3.9279	2.3467
0.4	973.3	0.6716	137.26	0.6996	15304.74	3.9277	2.3709
0.5	981.3	0.6780	138.17	0.6941	15582.54	3.9392	2.3872
0.6	996.7	0.6848	138.99	0.6723	16373.63	3.9397	2.3847
0.7	1005.2	0.6906	140.00	0.6574	17040.75	3.9539	2.3822
0.8	1011.3	0.6995	140.36	0.6490	17378.69	3.9496	2.3989

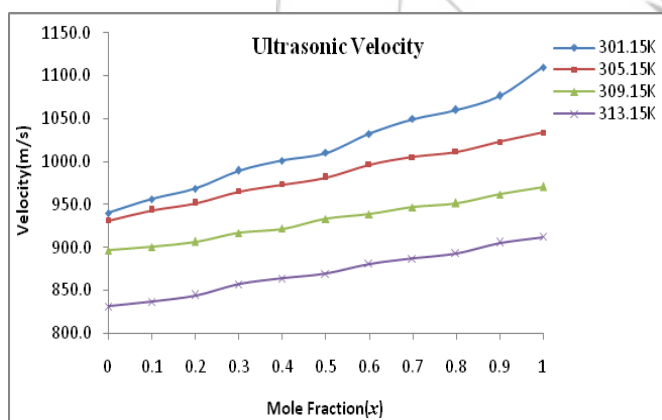
0.9	1023.0	0.7058	141.24	0.6431	17676.83	3.9563	2.4176
1.0	1034.0	0.7132	141.88	0.6466	17567.66	3.9563	2.4561

**Table-3:** For binary liquid mixture containing Triethylamine in n-hexane at 309.15K.

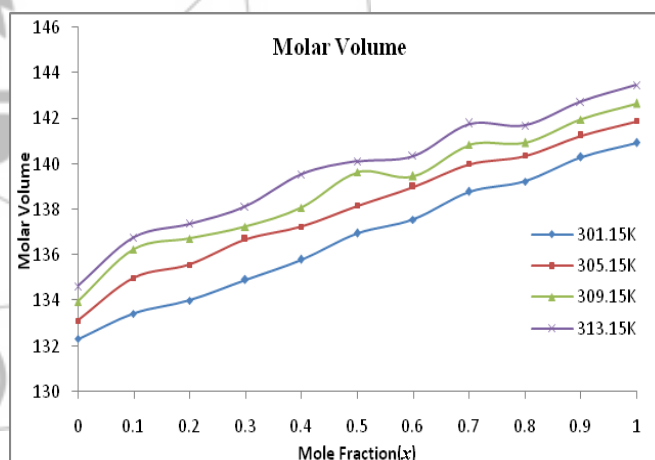
Mole Fraction (x)	U (ms <sup>-1</sup> )	$\rho \times 10^{-3}$ (Kg m <sup>-3</sup> )	V <sub>m</sub> (m <sup>3</sup> )	$T \times 10^{-14}$ (s)	R	W	H × 10 <sup>7</sup> KJ mole <sup>-1</sup>
0.0	896.7	0.6433	133.96	0.7701	13318.99	3.9485	2.3908
0.1	901.0	0.6435	136.25	0.7602	13847.38	4.0104	2.3299
0.2	906.7	0.6522	136.74	0.7605	13922.94	4.0099	2.3596
0.3	917.2	0.6607	137.25	0.7459	14326.57	4.0042	2.3747
0.4	922.0	0.6675	138.1	0.7383	14642.93	4.0171	2.3866
0.5	933.3	0.6709	139.64	0.7352	14894.08	4.0449	2.4018
0.6	938.5	0.6825	139.46	0.7193	15316.41	4.0233	2.4171
0.7	946.7	0.6865	140.84	0.7046	15965.14	4.0497	2.4105
0.8	951.5	0.6967	140.93	0.7011	16062.94	4.0379	2.4399
0.9	962.1	0.7022	141.96	0.6946	16373.11	4.0499	2.4546
1.0	970.5	0.7093	142.66	0.6986	16276.26	4.0538	2.4923

**Table 4:** For binary liquid mixture containing Triethylamine in n-hexane at 313.15K.

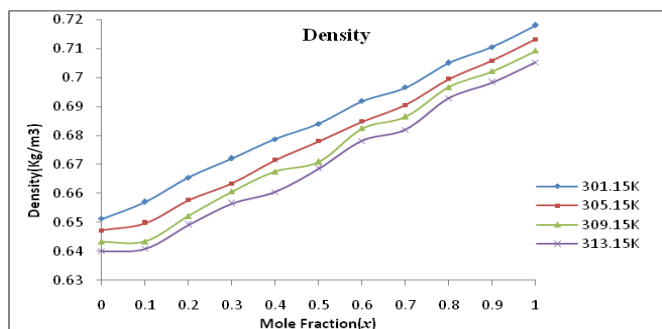
Mole Fraction (x)	U (ms <sup>-1</sup> )	$\rho \times 10^{-3}$ (Kg m <sup>-3</sup> )	V <sub>m</sub> (m <sup>3</sup> )	$T \times 10^{-14}$ (s)	R	W	H × 10 <sup>7</sup> KJ mole <sup>-1</sup>
0.0	831.2	0.6401	134.63	0.8622	11766.8	4.0582	2.4053
0.1	837.0	0.641	136.78	0.8517	12223.13	4.1138	2.3958
0.2	844.2	0.6491	137.39	0.8298	12743.03	4.1147	2.3976
0.3	857.0	0.6565	138.13	0.8167	13053.82	4.1123	2.418
0.4	864.0	0.6605	139.56	0.8075	13442.03	4.1419	2.4214
0.5	869.5	0.6686	140.12	0.813	13336.83	4.1437	2.4611
0.6	881.2	0.6781	140.37	0.7887	13905.69	4.1157	2.4681
0.7	887.0	0.682	141.76	0.7768	14388.03	4.1565	2.4554
0.8	893.3	0.6929	141.7	0.76	14802.75	4.137	2.48
0.9	905.2	0.6983	142.75	0.7526	15088.96	4.1473	2.4973
1.0	912.5	0.7053	143.47	0.763	14832.87	4.1527	2.5437



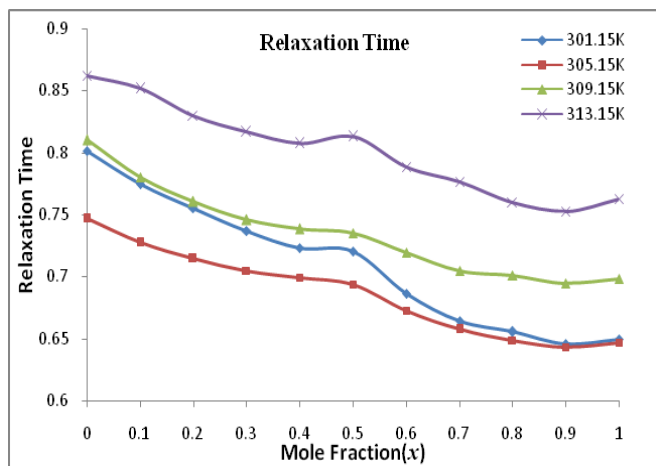
**Figure 1:** Variation of Ultrasonic Velocity with mole fraction for binary liquid mixture containing Triethylamine in n-hexane at 301.15K, 305.15K, 309.15K, 313.15K.



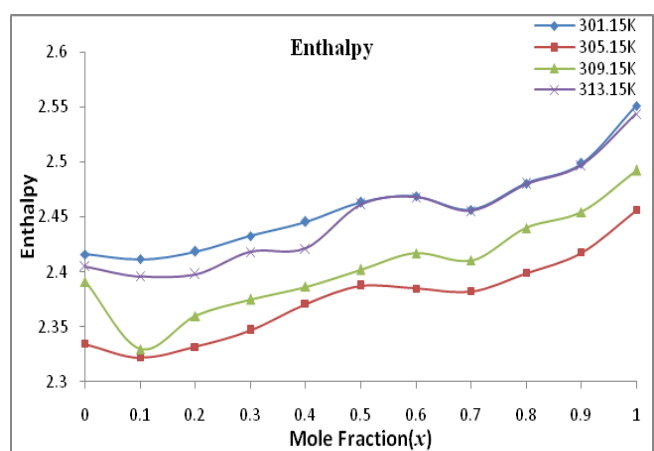
**Figure 3:** Variation of Molar Volume with mole fraction for binary liquid mixture containing Triethylamine in n-hexane at 301.15K, 305.15K, 309.15K, 313.15K.



**Figure 2:** Variation of Density with mole fraction for binary liquid mixture containing Triethylamine in n-hexane at 301.15K, 305.15K, 309.15K, 313.15K.



**Figure IV:** Variation of Relaxation time with mole fraction for binary liquid mixture containing Triethylamine in n-hexane at 301.15K, 305.15K, 309.15K, 313.15K.



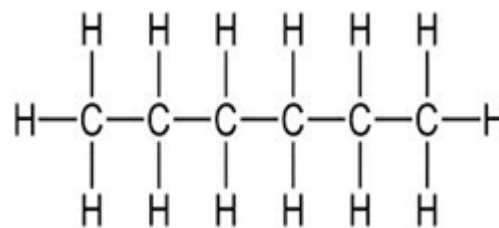
**Figure V:** Variation of enthalpy with mole fraction for binary liquid mixture containing Triethylamine in n-hexane at 301.15K, 305.15K, 309.15K, 313.15K.

The ultrasonic velocity increases with increase in concentration of triethylamine in n-hexane system at various temperature. This trend suggests that dipole – induced dipole interaction in higher concentration of triethylamine in binary mixture. When the temperature is increased in triethylamine – n-hexane system, the ultrasonic velocity decreases. This trend travels that at higher temperature the molecular interaction between the components are low.

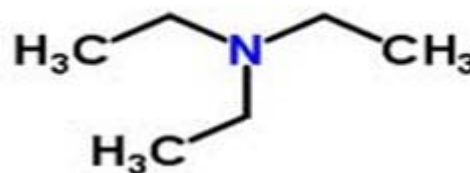
The relaxation time decreases with increasing concentration in the system. The dispersion of the ultrasonic velocity in the system should not contain information about the characteristic time ( $\tau$ ) of the relaxation process that causes dispersion. The relaxation time which is in the order of  $10^{-14}$  sec is due to structural relaxation process [25] and in such a situation it is suggested that the molecules get rearranged due to co-operative process [18].

Rao's constant ( $R$ ) and Wada's constant ( $W$ ) shows linear variation for the binary mixtures triethylamine – n-hexane systems predicting the absence of complex formation and only weak interaction exists in all these cases. Molar volume ( $V_m$ ) values remain constant for the binary mixture triethylamine – n-hexane systems.

## 5. Conclusion



n-hexane



Triethylamine

The acoustic data of Ultrasonic velocity ( $u$ ), viscosity ( $\eta$ ), density ( $\rho$ ) and related thermodynamic parameters with their values for binary liquid mixture over the whole concentration range of triethylamine in n-hexane may suggest the existence of a intermolecular interaction between its constituents.

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