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Thermo acoustical study of tetrahydrofuran with ethanol using ultrasonic technique at 323K

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ABSTRACT

The density, ultrasonic velocity and viscosity at the temperature 323K and at 3MHz frequency have been measured in the binary system of Tetrahydrofuran (THF) with the aliphatic alcohol Ethanol. When two or more liquids are mixed, there occur some changes in physical and thermodynamic properties because of change in free volume, change in energy and change in molecular orientations. Thermodynamic and acoustical parameters like adiabatic compressibility, intermolecular free length, specific acoustical impedance, Gibbs energy, relaxation time, free volume and internal pressure are of considerable interest in understanding the inter-molecular interactions in binary liquid mixtures. Using measured values of ultrasonic velocity, density and viscosity, following evaluated different acoustical interaction parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f), specific acoustical impedance (Za), relaxation time (τ), Gibbs energy (ΔG), free volume (V_f) and internal pressure (πi) can be used to study the Physico-chemical behavior and molecular interactions in pure liquids, liquid mixtures and the solutions. From these acoustical parameters, the nature and the strength of molecular interactions in the binary system of Tetrahydrofuran (THF) + Ethanol are discussed.

Keywords: Ultrasonic velocity, Acoustical parameters, adiabatic compressibility, free length, free volume internal pressure, Molecular interactions, binary liquid mixture, Tetrahydrofuran and Ethanol.

INTRODUCTION

The ultrasonic study of inter molecular interactions plays an important role in the development of molecular sciences. In the recent years, ultrasonic technique has become more powerful tool in providing information regarding the behavior of liquids and solids owing to its ability of characterizing physiochemical behavior of the medium [1-3]. Ultrasonic velocity measurements are useful in the field of interactions and structural aspect studies, for characterizing the Physico-chemical behavior of liquid mixtures [4-7]. Ultrasonic measurements of acoustic parameters with change in mole fraction give an insight in to the molecular process [8-11]. This type of study has increased in recent years due to industrial applications. Many researchers have undertaken these studies qualitatively through ultrasonic velocity, adiabatic compressibility and viscosity measurements [12-16]. The Tetrahydrofuran (C_4H_8O) is used as a solvent in chemical synthesis, used in the preparation of chemicals, insecticides, fabrication of materials for food packaging, transport and storage. It is used for Polymers, adhesive, magnetic strips, printing ink and for Grignard & metal hydroxide reactions. It is toxic in nature. Ethanol (CH_3CH_2OH) is used as a solvent, used in the manufacture of varnishes & perfumes, used as preservative for biological specimen, used in explosives, automotive fuel industry, drug applications. It is volatile, flammable and colorless. Tetrahydrofuran and aliphatic alcohol Ethanol is versatile fluid and has been used on a wide range of fields and applications**.**

In view of extensive applications of Tetrahydrofuran & ethanol in the engineering process, pharmaceutical industries, present study provides qualitative information regarding the nature and strength of molecular interactions in the liquid mixture of Tetrahydrofuran + Ethanol at the temperature 323K through the derived parameters from ultrasonic velocity, density & viscosity measurement. The present investigation is undertaken, in order to study the dependence of the relative strength of intermolecular interaction and their nature in pure liquids and liquid mixtures. The results are discussed in terms of molecular interactions.

2. Theory:

i. Adiabatic compressibility (β_a**)**:

$$\beta_a = 1/ (U^2 * \rho) \quad (1)$$

ii. Intermolecular free length (L_f**)**:

$$L_f = K_J (\beta_a)^{1/2} \quad (2)$$

Where K_J is the temperature dependent Jacobson's constant [17, 18**]** but independent of the nature of liquid.

iii. Relaxation time (τ):

Relaxation time (τ) is the time taken for the excitation energy to appear as translational energy and it depends on temperature and on impurities. The dispersion of ultrasonic velocity in binary mixture reveals information about the characteristic time of the relaxation process that causes dispersion. The relaxation time (τ) can be calculated from the relation as;

$$\tau = (4/3) \beta_a * \eta. \quad (3)$$

iv. Acoustic impedance (Za):

$$Za = U * \rho. \quad (4)$$

v. Gibb's free energy (ΔG):

The relaxation time for a given transition is related to the activation energy. The variation of relaxation time (τ) with temperature (T) can be expressed in the form of Eyring self process theory.

$$1/ \tau = [(K_B T) / h] * \exp (-\Delta G/K_B T). \quad (5)$$

The above equation can be rearranged as,

$$\Delta G = (- K_B T) \log [h/ (K_B T \tau)]. \quad (6)$$

or,

$$\Delta G = (K_B T) \log [(K_B T \tau)/h]. \quad (7)$$

Where K_B is the Boltzmann's constant ($1.3806 \times 10^{-23} Jk^{-1}$), h is the plank's constant

6.63×10^{-34} JS), T is the absolute temperature and τ is the relaxation time.

vi. Free Volume (V_f) :

$$V_f = [(Me_{ff} U) / (K \eta)]^{3/2} \quad (8)$$

Where, Meff (Effective mass) = Σ mi xi, in which mi and xi are the molecular weight and the mole fraction of the individual constituents respectively. K is the temperature independent constant, which is equal to $4.28 * 10^9$ for all liquids and η be the viscosity.

vii. Internal pressure (π_i):

$$\pi_i = (b RT)[(K * \eta) /(U)]^{½} * [(\rho^{2/3}) / (Me_{ff}^{7/6})] \quad (9)$$

Where, b is the cubic packing which is assumed to be 2 for all liquids and solutions, K is the temperature independent constant ,T is the absolute temperature, R is universal gas constant, η be the viscosity and M_{eff} the effective molecular weight .

MATERIALS AND METHODS

The liquids were of Analar grade and redistilled before use. The binary mixture of different mole fractions of the two components, namely Tetrahydrofuran and Ethanol were prepared immediately before use. The velocity of Ultrasonic wave (U) at frequency 3MHz and density (ρ) in the mixtures were measured by Ultrasonic Multifrequency Interferometer (Model-Mittal M-83) and using pycknometer by relative measurement method with an accuracy of ±0.1Kgm^{-3}. The Digital thermostat maintains the temperature constant of the samples, by circulating water through double walled measuring cell made up of steel containing experimental solution of different molarities at the desired temperature. An Ostwald's viscometer (calibrated) was used for viscosity (η) measurement of pure liquids and liquid mixtures with accuracy of ±0.0001 Ns/m^2. The setup is checked for standard liquids. All the precautions were taken to minimize the possible experimental error.

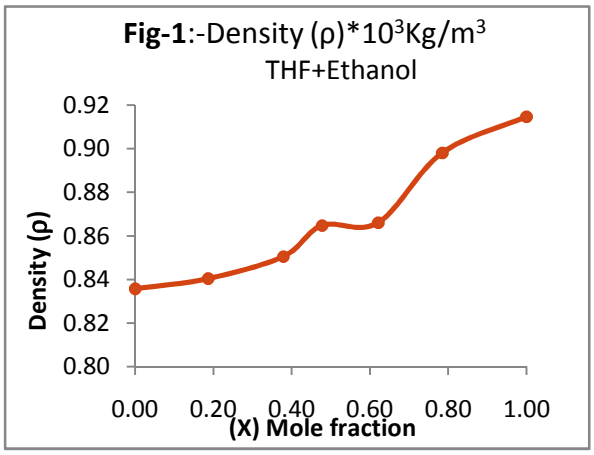
Table-1:– Shows Density (ρ), Ultrasonic Velocity (U), Viscosity (η) and adiabatic compressibility (β_a) of Binary system Tetrahydrofuran + Ethanol at 323K

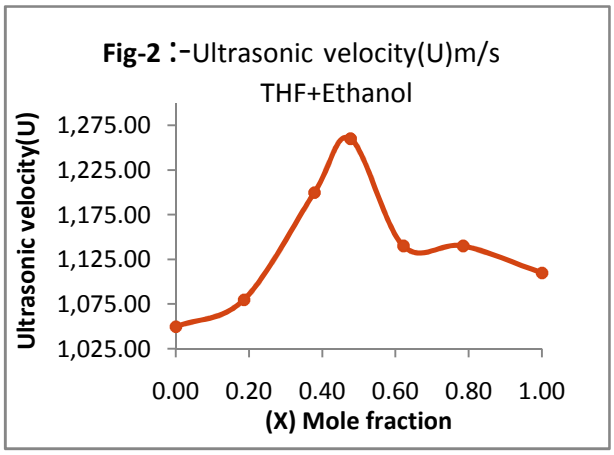
Mole fraction (X) of THF in ethanol	Density(ρ) (10^3kgm^{-3})	Ultrasonic Velocity(U) (m/s)	Viscosity(η) (10^{-3} Nsm^{-2})	Adiabatic compressibility(β_a) (10^{-10}m^{2}N)
0	0.8356	1050.00	0.5372	0.7579
0.1859	0.8403	1080.00	0.4882	0.7204
0.3785	0.8505	1200.00	0.4378	0.5906
0.4774	0.8647	1260.00	0.4119	0.5446
0.6215	0.8661	1140.00	0.3741	0.6664
0.7851	0.8981	1140.00	0.3313	0.6910
1	0.9147	1110.00	0.2751	0.7423

Table-2:- Shows Free length (L_f), relaxation time(τ), Gibb's free energy(ΔG), Acoustic Impedance (Za), Free Volume (V_f) and Internal Pressure (πi) for the binary system: THF + Ethanol at 323K

Mole fraction (X) of THF	Free length(L_F) (10^{-10}m)	Relaxation time(τ) (10^{-12}s)	Gibb's free energy(ΔG) 10^{-20} (KJmole^{-1})	Acoustic impedance(Za) (10^6kg/m^{2}s)	Free Volume (V_f) 10^{-8} (m^{3}mol^{-1})	Internal Pressure (πi) 10^6 (P_a.S)
0	0.5676	0.5426	1.1427	0.8773	9.6557	6.3607
0.1859	0.5534	0.4690	1.1144	0.9075	13.4943	5.3824
0.3785	0.5012	0.3447	1.0548	1.0206	21.4313	4.4397
0.4774	0.4811	0.2991	1.0273	1.0895	27.0333	4.1210
0.6215	0.5322	0.3324	1.0478	0.9873	29.4998	3.8533
0.7851	0.5422	0.3052	1.0312	1.0238	39.1015	3.6090
1	0.5617	0.2722	1.0091	1.0153	56.0766	3.1449

Graphs: (Fig. 1-10), shows the graph of the density, Ultrasonic velocity, viscosity, adiabatic compressibility, free length, relaxation time, Gibb's free energy, acoustical impedance, free volume and internal pressure at the temperature 323K





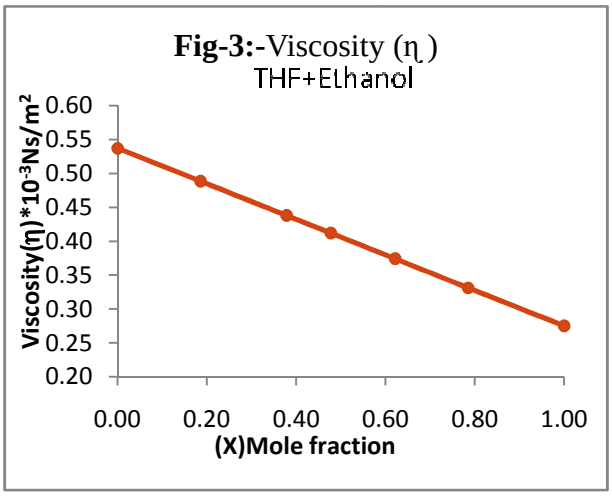


Fig-3:-Viscosity (η)
THF+Ethanol
Viscosity(η)*10-3Ns/m2
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.00
0.20
0.40
0.60
0.80
1.00
(X)Mole fraction

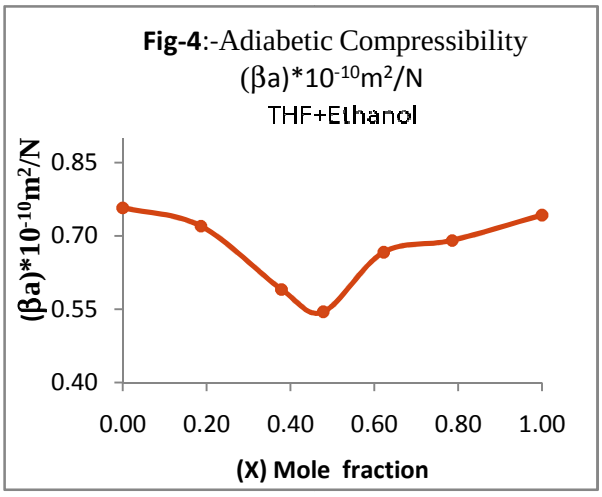


Fig-4:-Adiabetic Compressibility
(βa)*10-10m2/N
THF+Ethanol
(βa)*10-10m2/N
0.85
0.70
0.55
0.40
0.00
0.20
0.40
0.60
0.80
1.00
(X) Mole fraction

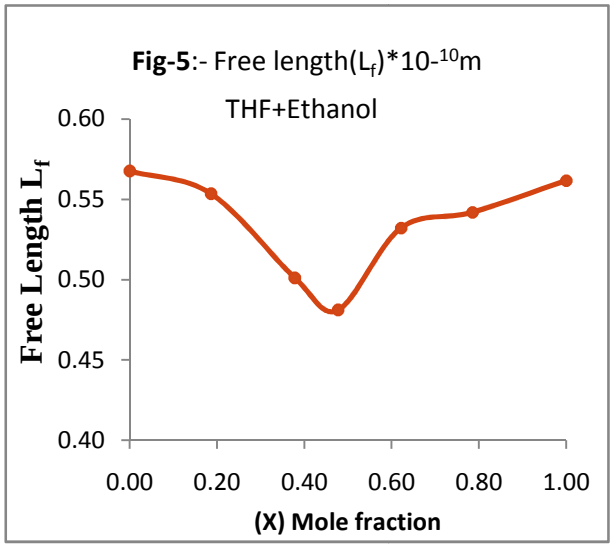


Fig-5:- Free length(Lf)*10-10m
THF+Ethanol
Free Length Lf
0.60
0.55
0.50
0.45
0.40
0.00
0.20
0.40
0.60
0.80
1.00
(X) Mole fraction

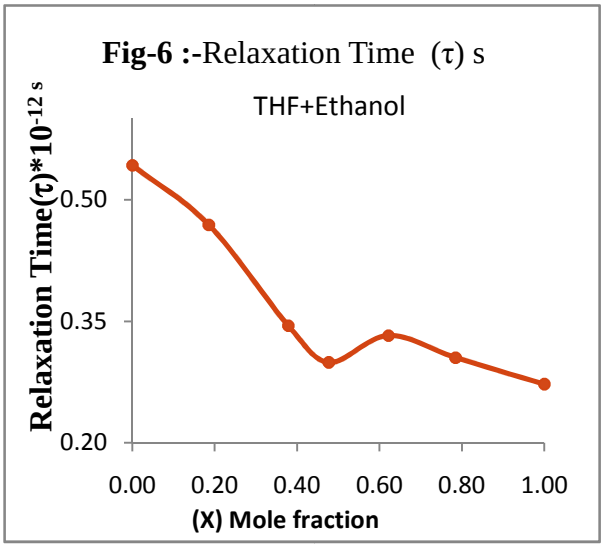


Fig-6 :-Relaxation Time (τ) s
THF+Ethanol
Relaxation Time(τ)*10-12 s
0.50
0.35
0.20
0.00
0.20
0.40
0.60
0.80
1.00
(X) Mole fraction

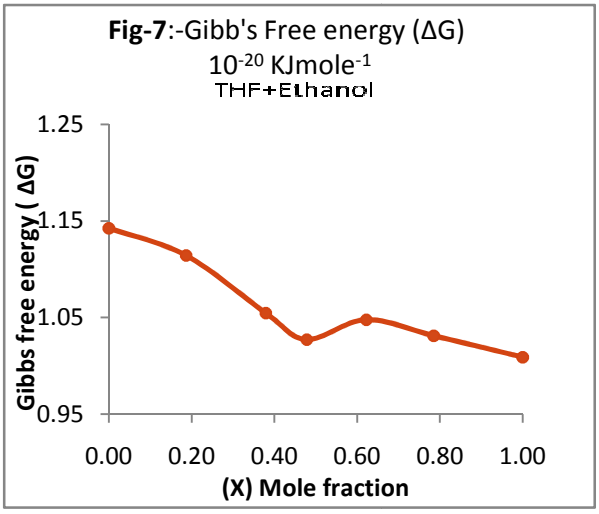


Fig-7:-Gibb's Free energy (ΔG)
10-20 KJmole-1
THF+Ethanol
Gibbs free energy (ΔG)
1.25
1.15
1.05
0.95
0.00
0.20
0.40
0.60
0.80
1.00
(X) Mole fraction

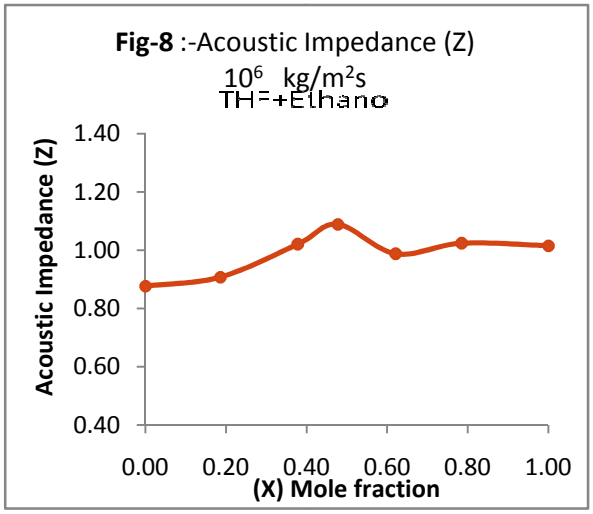
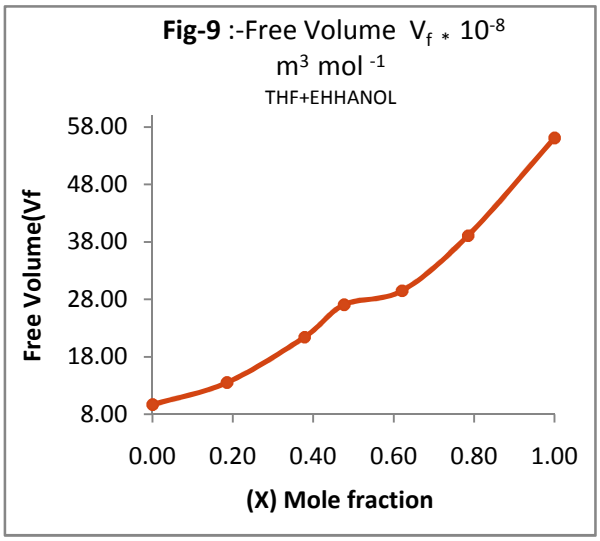
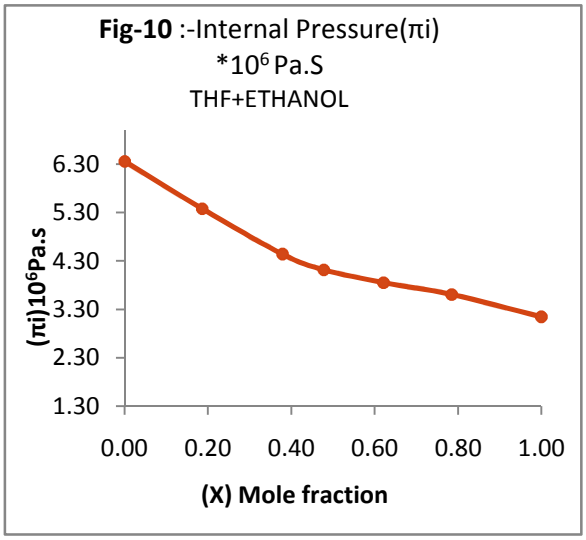


Fig-8 :-Acoustic Impedance (Z)
10⁶ kg/m²s
THF+Ethano
Acoustic Impedance (Z)
1.40
1.20
1.00
0.80
0.60
0.40
0.00
0.20
0.40
0.60
0.80
1.00
(X) Mole fraction





RESULTS AND DISCUSSION

Experimental density, viscosity and ultrasonic velocity values and adiabatic Compressibility for the binary system: Tetrahydrofuran + Ethanol at 323K are given in the Table-1. The parameters free length (L_f), acoustic impedance (Za), relaxation time (τ), Gibb's free energy (ΔG), Free Volume (V_f) and Internal Pressure (πi) at temperature 323K are listed in Table–2. The variation of density, viscosity, Ultrasonic velocity, adiabatic compressibility**,** free length, acoustic impedance, relaxation time , Gibb's free energy, Free Volume and internal pressure Vs mole fraction of Tetrahydrofuran in ethanol at 323K are shown in the graphs (fig. 1 to 10**)** respectively.

From the Table–2, it is noted that, the density (ρ) increases with increase in mole fraction of Tetrahydrofuran in ethanol for the systems. Ultrasonic velocity increases and viscosity decreases with increase in mole fraction of the solute in the systems. It has been observed that for a given concentration, as the number of CH-group or Chain length changes, the sound velocity changes. This may lead to the presence of specific molecular interaction between the molecules of the liquid mixture. The adiabatic compressibility and free length are the deciding factors of the ultrasonic velocity in the liquid systems. It represents the presence of weak interaction between the solute and solvent molecules. Acoustic impedance (Za) increases with increase in the mole fraction of the solute in the systems. The relaxation time (τ) decreases with increasing the mole concentration of the solute in systems. The dispersion of the ultrasonic velocity in the system may contain information about the characteristic time (τ) of the relaxation process that causes dispersion. The relaxation time which is in the order of 10^{-12} sec., is due to structural relaxation process [19] and in such a situation, it is suggested that, the molecules get rearranged due to co-operative process [20].

The Gibb's free energy (ΔG) decreases with increasing mole fraction the solute in the systems. This may be due to the intermediate compound formation between the binary liquids. It is observed that, generally the decrease in Gibb's free energy favors the formation of product from reaction. This observation confirms the formation of hydrogen bonding in the binary mixture. Fig. 9 and 10 contain the plots of free volume (V_f) and internal pressure (πi) versus mole concentration. It is observed that free volume increases and internal pressure decreases with increase in molar concentration of tetrahydrofuran in ethanol indicating increase in dipole association in the molecules of the components. Such behavior of free volume and internal pressure generally indicates the association through hydrogen bonding. This suggests the close packing of the molecules inside the shield.

CONCLUSION

The molecular interactions present in Tetrahydrofuran with ethanol as a solvent have been studied by viscosity, density and ultrasonic velocity study. Solute-solvent and dipole- dipole type interactions for the systems have been estimated based on Gibb's free energy calculations using data on viscosity and ultrasonic velocity of the solutions at 323K temperature. The result indicates the existence of molecular interaction between the solute and the solvent in their solutions. The result is also shows the presence of higher degree of molecular interaction between Tetrahydrofuran and ethanol in solution. It has been observed that, weak dispersive type intermolecular interactions are confirmed in the system investigated. The nonlinear behavior of these parameters provides the knowledge about various interactions among the molecules. The changes in the nature and degree of molecular interactions in

different concentration of the binary system:-Tetrahydrofuran + Ethanol, depends upon the nature of solvent, the structure of solute molecule and extent of solution taking place in the solution.

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