International Journal for Pharmaceutical Research Scholars (IJPRS)

V-3, I-1, 2014 ISSN No: 2277 - 7873

RESEARCH ARTICLE

Molecular Interaction Study of Binary Liquid Mixture of Tetrahydrofuran and Ethanol at 313K

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Manuscript No: IJPRS/V3/I1/00079, Received On: 13/02/2014, Accepted On: 25/02/2014

ABSTRACT

The molecular interaction study in the binary liquid mixture of tetrahydrofuran (THF) with ethyl Alcohol (Ethanol) in mole fraction has been carried out at 313K using Ultrasonic measurement technique. The experimental density (ρ), Ultrasonic velocity (U) and viscosity (η) at 313K was measured. From the experimental data, various acoustical parameters such as, adiabatic compressibility (βa), intermolecular free length (L_f) and acoustical impedance (Z) were calculated. Weak dispersive type inter molecular interactions were confirmed in the system investigated. Also thermodynamic parameters like relaxation time (τ), Gibbs energy (ΔG) were calculated, from which, the nature & strength of molecular interactions in the binary system are discussed. The results are interpreted in terms of molecular interactions between the components of mixture.

KEYWORDS

Ultrasonic velocity, Acoustical parameters, Molecular interactions, Binary liquid mixtures, Tetrahydrofuran and Ethanol

INTRODUCTION

The ultrasonic study of intermolecular interactions plays an important role in the development of molecular sciences.[1] In recent years ultrasonic technique has become powerful tool in providing information regarding the behaviour of liquids and solids owing to its ability of characterizing physiochemical behaviour of the medium.[2,3] Many researchers have undertaken these studies qualitatively through ultrasonic velocity, adiabatic compressibility and viscosity measurements for liquid mixtures,[4,5,6,7] binary and ternary mixtures[8,9].

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Ultrasonic velocity measurements are useful in the field of interactions and structural aspect studies, for characterizing the Physico-chemical behaviour of liquid mixtures.[10,11] Ultrasonic measurements of acoustic parameters with change in mole fraction give an insight in to the molecular process.[12,13,14] This type of study has increased in recent years due to industrial applications.

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. The 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. The tetrahydrofuran and Ethanol are versatile fluid and have been used on a wide range of fields and applications. In the view of extensive applications of tetrahydrofuran and 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 313K through derived parameters from the ultrasonic velocity, density and viscosity measurements. Results are analysed in the light of molecular interactions in the binary liquid mixtures.

Theory

Adiabatic Compressibility (β_a)

The adiabatic compressibility (βa) has been calculated from the ultrasonic velocity (U) and the density (ρ) of the medium using the equation as:

$$\beta_a = 1/ (U^2 * \rho) \text{ ---------- (1)}$$

Intermolecular Free Length (L_f)

Intermolecular free length has been determined as:

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

Where K_J is the temperature dependent Jacobson's constant but independent of the nature of liquid.

Free Volume (V_f)

The free volume has been calculated in terms of ultrasonic velocity (U) and viscosity (η) of the liquid as:

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

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.

Internal Pressure (πi)

On the basis of statistical thermodynamics, derived an expression for the determination of internal pressure (π_i) by the use of free volume concept as:

$$\pi i = (b\ RT)[(K * \eta) /(U)]^{½} * [(\rho^{2/3}) / (Me_{ff}^{7/6})] \text{ ---------- (4)}$$

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 Meff the effective molecular weight .

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;

$$\boldsymbol{\tau} = (4/3)\ \beta a * \eta. \text{ ---------- (5)}$$

Where βa and η are adiabatic compressibility and viscosity of the liquid and liquid mixtures.

Acoustic Impedance (Za)

The specific acoustic impedance is given by,

$$Za = U * \rho. \text{ ----------(6)}$$

Where U and ρ are the ultrasonic velocity and density of the liquid respectively.

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.

$$1/\tau = [(K_B T) /h] * \exp (-\Delta G/K_B T) \text{ ---------- (7)}$$

The above equation can be rearranged as,

$$\Delta G = (- K_B T) \log [h/ (K_B T\tau) \text{ --------- } (8)$$

$$\text{or, } \Delta G = (K_B T)\log [(K_B T\tau)/h] \text{ ---------- } (9)$$

Where K_B is the Boltzmann's constant (1.3806×10^{-23} Jk^{-1}), h is the plank's constant $6.63*10^{-34}$ JS), T be the absolute temperature and τ be the relaxation time.

Experimental Details

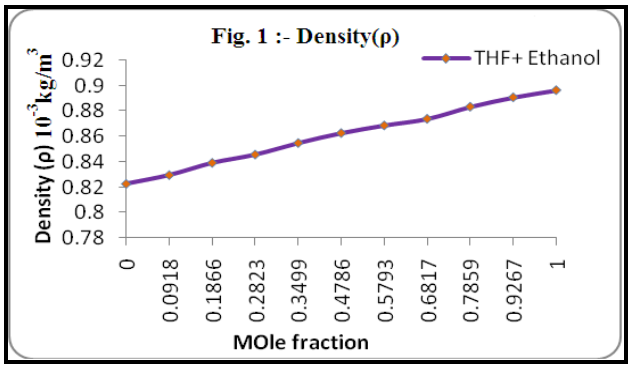
The liquids were of Analar grade and redistilled before use. The binary mixture of different mole fractions of the two components namely Tetrahydrofuran and Ethanol were prepared immediately before use. The velocity of Ultrasonic wave (U) at frequency 3MHz and density (ρ) in the mixtures were measured by Ultrasonic Multifrequency Time Interferometer (Model-Mittal M-83) and Thermostat (digital) maintains the temperature of samples, by circulating water through double walled measuring cell made up of steel containing experimental solution of different molality at the desired temperature, constant up to 0.1^0C. A specially designed and fabricated double walled, metallic Ultrasonic cell & glass cell along with 6 digit monopan balance having accuracy of 1 in10^4 ± 1 m/s in velocity and 1 in10^4 gm in density measurement is used. An Ostwald's viscometer (calibrated) was used for viscosity (η) measurement of pure liquids and liquid mixtures with accuracy of ±0.001 Ns/m^2. All the necessary precautions were taken to minimise the possible experimental error.

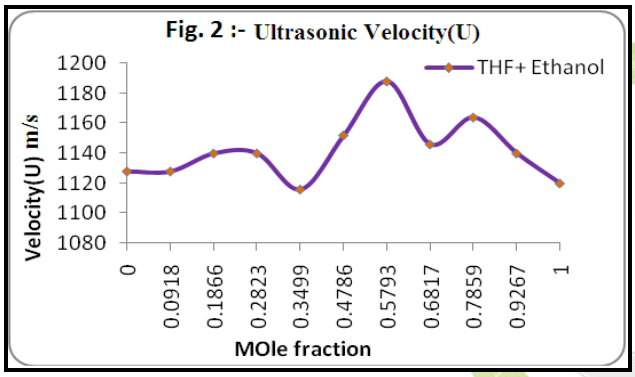
Experimental Data

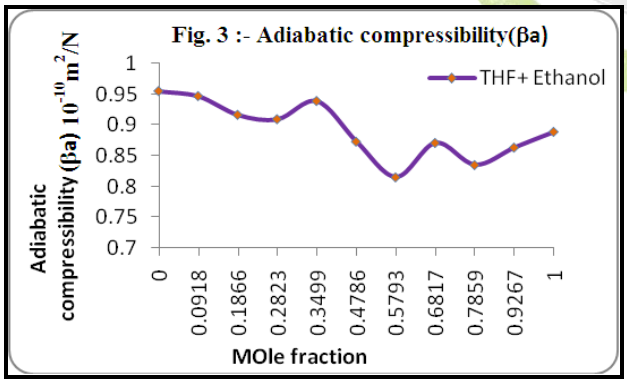
Table 1: Density (ρ), Ultrasonic Velocity (U), Adiabatic compressibility (βa) , Viscosity (η), Free length (L_f), Gibb's free energy(ΔG), Acoustic impedance (Z) and relaxation time(τ) of binary system: Tetrahydrofuran + Ethanol at 313K

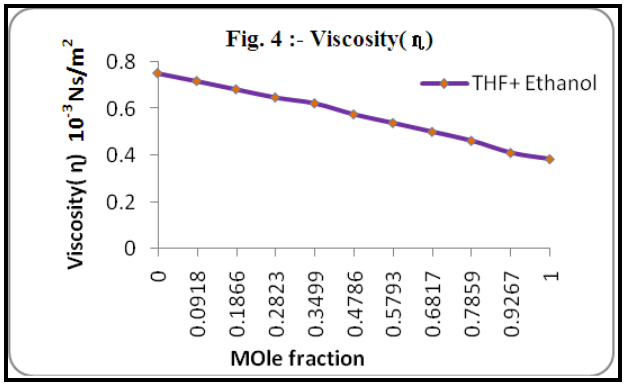
Mole fraction (X) of THF	Density (ρ) (kgm^{-3})	Ultrasonic Velocity (U) m/s	Adiabatic compressibility(βa) $10^{-10}m^2N^{-1}$	Viscosity (η) 10^{-3} Nsm^{-2}	Free length(L_F) 10^{-10}m	Gibb's free energy (ΔG)10^{-20} $KJmole^{-1}$	Acoustic impedance(Z) $10^6kg/m^2$ s	Relaxation time (τ) 10^{-12}s
0	822.70	1128.00	0.9553	0.7518	0.6274	1.208	0.9280	0.9575
0.0918	829.60	1128.00	0.9473	0.7181	0.6248	1.197	0.9357	0.9070
0.1866	839.20	1140.00	0.9169	0.6833	0.6147	1.182	0.9566	0.8354
0.2823	845.70	1140.00	0.9098	0.6482	0.6123	1.171	0.9640	0.7863
0.3499	854.81	1116.00	0.9393	0.6234	0.6222	1.169	0.9539	0.7808
0.4786	862.62	1152.00	0.8735	0.5762	0.6000	1.141	0.9937	0.6711
0.5793	868.61	1188.00	0.8157	0.5393	0.5798	1.116	1.0318	0.5865
0.6817	873.83	1146.00	0.8714	0.5017	0.5992	1.114	1.0013	0.5829
0.7859	883.32	1164.00	0.8356	0.4635	0.5868	1.092	1.0281	0.5164
0.9267	890.73	1140.00	0.8639	0.4118	0.5967	1.076	1.0153	0.4744
1	896.34	1120.00	0.8894	0.3852	0.6054	1.068	1.0038	0.4565

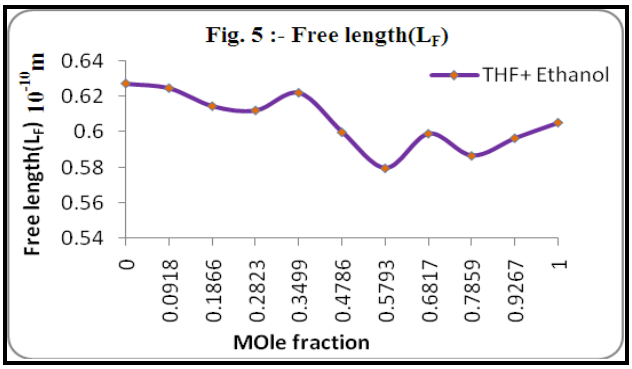
Graph: The variation of density, ultrasonic velocity, adiabatic compressibility, viscosity, free length, Gibb's free energy, acoustic impedance and relaxation time Vs mole fraction of Tetrahydrofuran(THF) for the binary system: Tetrahydrofuran +Ethanol at 313K are shown in the Graphs (fig.-1 to 8).

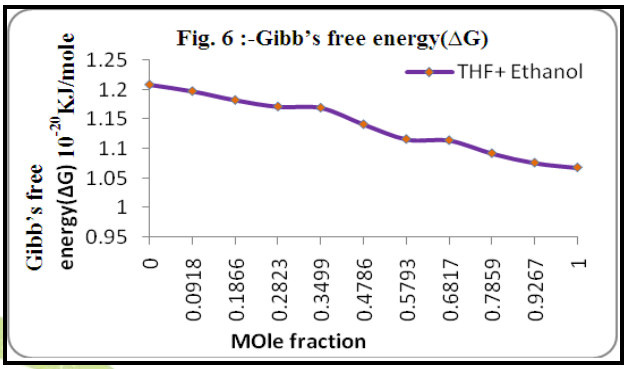


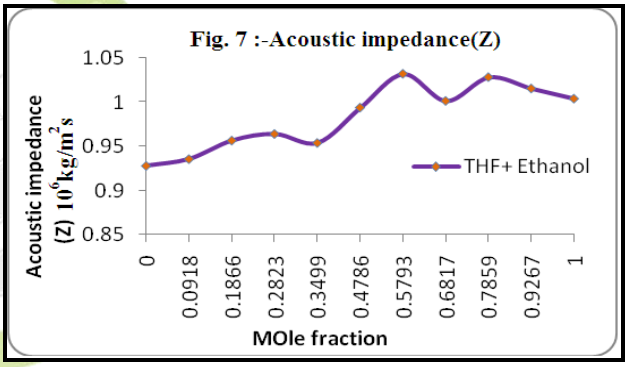


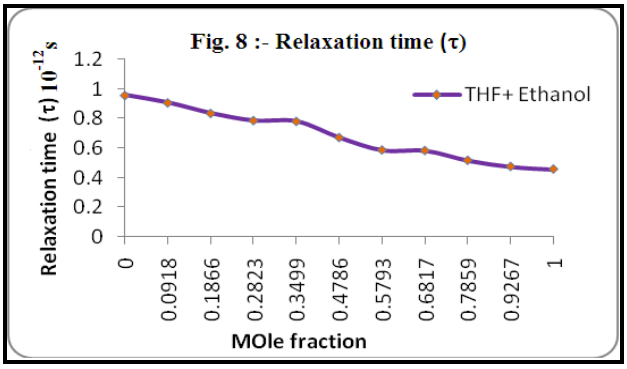












RESULTS AND DISCUSSION

Using the experimental data of ultrasonic velocity (U), density (ρ) and viscosity (η), various acoustical parameters such as temperature dependent adiabatic compressibility (βa), intermolecular free length (L_f), acoustical impedance (Z), relaxation time (τ) and Gibbs

energy ((ΔG) were calculated by using following standard equations as shown in the theory.

Experimental values of density, viscosity, velocity and adiabatic compressibility, Free length (L_f), Gibb's free energy (ΔG), Acoustic impedance (Z) and relaxation time (τ) for the binary system (Tetrahydrofuran+ Ethanol) at 313K are given in Table-1. The variation of density, viscosity , ultrasonic velocity, adiabatic compressibility, free length, Gibb's free energy, relaxation time and acoustic impedance Vs mole fraction of Tetrahydrofuran(THF) for the binary system: Tetrahydrofuran +Ethanol at 313K are shown in the Graphs (fig.-1-8). From the Table-1, it is observed that, the density (ρ) increases with increase in mole fraction for the system: Tetrahydrofuran + Ethanol and ultrasonic velocity decreases with increasing mole fraction for the system. This increase in structural order of ethanol may result in more cohesion, and leads to a decrease in β_a. The decreases in ultrasonic velocity are due to the decrease in adiabatic compressibility and free length of the liquid mixtures. This may lead to the presence of dispersive force (London force) between the molecules of the liquid mixture. The adiabatic compressibility and intermolecular free length are the deciding factors of ultrasonic velocity in the binary liquid mixtures. The decrease in free length represent that, there is weak interaction between the molecules of the mixture and the molecules are nearer in the system.

The relaxation time (τ) decreases with increase in mole fraction, which is in the order of 10^{-12} sec., is due to structural relaxation process and in such a situation, it is suggested that, the molecule gets rearranged due to co-operative process. The Gibb's free energy (ΔG) decreases with increase in mole fraction of tetrahydrofuran, which may due to intermediate compound formation between the binary liquid mixtures**.**

CONCLUSION

The ultrasonic velocity, density and viscosity have been measured for ethanol in the solution of tetrahydrofuran at the temperature 313K. The variation of ultrasonic velocity, density, viscosity and other related parameters such as adiabatic compressibility, intermolecular free length, acoustic impedance, Gibb's free energy and relaxation time of ethanol at various concentrations in tetrahydrofuran shows the variation to be increased and decreased nonlinearly. Consequently ultrasonic velocity of the systems decreases depending on the structural properties of the solute.

It is clear that solute causing electrostriction lead to decrease in the compressibility of the solution. Hydrophilic solutes often show negative compressibility, due to ordering that is induced by them in tetrahydrofuran structure. The solute that decreases the ultrasonic velocity is of structure braker. The nonlinearity confirms the presence of solute-solvent molecular interaction. The observed molecular interaction, complex formation and hydrogen bond formation are responsible for the hetero-molecular interaction in the liquid systems. This provides useful information about inter and intra molecular interactions of the mixture as existing in the liquid systems.

ACKNOWLEDGEMENT

The authors are thankful to Dr S V Moharil, Head of Department of Physics; RTM Nagpur University Nagpur and Dr S R Aswale, Principal L T M Wani for valuable guidance and constant encouragement.

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