

## Molecular interactions studies in liquid mixture using Ultrasonic technique

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### **Abstract**

*Density, viscosity and ultrasonic velocity have been measured for binary liquid mixtures containing Methylmethacrylate+2-Methoxy ethanol, Methylmethacrylate +2-Ethoxy ethanol, Methyl methacrylate+2 Butoxy ethanol at 303K. The adiabatic compressibility, free length, free volume, internal pressure, relaxation time, acoustic impedance and Gibbs's free energy values have been calculated from the experimental data. These parameters are used to discuss the molecular interactions in the mixtures.*

**Keywords:** *Acoustical Parameters, Binary system, Molecular interactions, Ultrasonic velocity.*

### **1. Introduction**

The study of intermolecular interaction plays an important role in the development of molecular sciences. A large number of studies have been made on the molecular interaction in liquid systems by various physical methods like Infrared [1,2], Raman effect [3,4], Nuclear Magnetic resonance, Dielectric constant[5], ultra violet[6] and ultrasonic method [7,8]. In recent years ultrasonic technique has become a powerful tool in providing information regarding the molecular behavior of liquids and solids owing to its ability of characterizing physiochemical behavior of the medium. The present investigation deals with the study of molecular interaction in 3 binary liquid mixtures (Methylmethacrylate+2MethoxyEthanol, Methylmethacrylate+2EthoxyEthanol, Methylmethacrylate+2ButoxyEthanol at 30° C).

Departure from linearity in the velocity versus concentration in liquid mixtures is taken as an indication of the existence of interaction between the different species. The physical and

chemical properties of liquid mixtures have been studied by numbers of workers [9,10] and they correlated the non-linear variation of ultrasonic velocity, compressibility and other related parameters with structural changes occurring in a liquid as its concentration is varied in a liquid mixture.

The intermolecular forces responsible for the molecular interactions can be classified as long range forces and Short range forces. The long range forces are the electrostatic induction and dispersion forces and they arise when the molecules come close enough together causing a significant overlap of electron clouds and are often highly directional.

The non-linear variation of adiabatic compressibility of the solution with concentration of the solute was qualitatively described to hydrogen bonding and their result confirms that the sign and magnitude of such deviation depends on the strength of interaction between unlike molecules.

Though spectroscopic methods play a major role in the molecular interaction studies, the non-spectral studies such as calorimetric, magnetic, ultrasonic velocity and viscosity measurements have also been widely used, in the elucidation of the formation of complexes.

In this report we have evaluated the acoustic Parameters, namely the Adiabatic Compressibility ( $\beta$ ), Free Length ( $L_f$ ), Free volume ( $V_f$ ), Internal Pressure ( $\pi_i$ ), Relaxation Time ( $\tau$ ), Acoustic Impedance ( $Z$ ) and Gibb's free energy ( $\Delta G^*$ ) for the binary mixtures Methylmethacrylate + 2-Methoxyethanol, Methylmethacrylate + 2-Ethoxyethanol, Methylmethacrylate + 2-Butoxy ethanol at 303K. The results are discussed in terms of molecular interactions.

## 2. Experimental techniques

### Theoretical Aspects

#### 1. Adiabatic compressibility ( $\beta$ )

The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. These changes are related to the compressibility of the medium by thermodynamic relation

$$\beta = \frac{1}{v} \left[ \frac{\delta_v}{\delta_p} \right] \quad (1)$$

It can also be calculated from the speed of sound ( $U$ ) and the density of the medium ( $\rho$ ) using the equation of Newton Laplace as

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

## 2. Intermolecular free length

The adiabatic compressibility of a liquid can be expressed in terms of the intermolecular free length which is the distance between the surfaces of the neighboring molecules and is given by the relation,

$$L_f = K_T \beta_{ad}^{\frac{1}{2}} \quad (3)$$

Where  $K_T$  is the temperature dependent constant.

## 3. Free Volume ( $V_f$ )

Free volume is one of the significant factors in explaining the variations in the physio-chemical properties of liquids and liquid mixtures. The free space and its dependent properties have close connection with molecular structure and it may show interesting features about interactions, which may occur when two or more liquids are mixed together. This molecular interactions between like and unlike molecules are influenced by structural arrangements along with shape and size of the molecules. A liquid may be treated as if it were composed of individual molecules each moving in a volume  $V_f$  in an average potential due to its neighbors. That is, the molecules of a liquid are not quite closely packed and there are some free space between the molecules for movement and the volume  $V_f$  is called the free volume [11]. Eyring and Kincaid [12] defined the free volume as the effective volume in which particular molecule of the liquid can move and obey perfect gas laws.

Free volume in terms of Ultrasonic velocity ( $U$ ) and the Viscosity of the liquid ( $\eta$ ) as

$$V_f = \left[ \frac{M_{eff} U}{K \eta} \right]^{\frac{3}{2}} \quad (4)$$

Where  $M_{eff}$  is the effective molecular weight ( $M_{eff} = \sum m_i X_i$  in which  $m_i$  and  $X_i$  are the molecular weight and the mole fraction of the individual constituents respectively).  $K$  is a temperature independent, constant which is equal to  $4.28 \times 10^9$  for all liquids.

## 4. Internal Pressure ( $\pi_i$ )

The measurement of internal pressure is important in the study of the thermodynamic properties of liquids. The internal pressure is the cohesive force, which is a resultant of force of attraction and force of repulsion between the molecules [13,14]. Cohesion creates a pressure within the liquid of value between 103 and 104 atmosphere. Internal pressure also gives an idea of the solubility characteristics. Dissolved solutes exist under the internal pressure of the medium and their interactions with the solvent arise through hydrogen bonding, charge transfer, Columbic (or) Vanderwaal's interaction. The term  $a/v^2$  in Vanderwaal's [15] equation being the measure of attractive force of the molecule is called the cohesive (or) internal pressure.

The internal pressure is the single factor which varies due to all type of solvent-solute, solute-solute and solvent-solvent interactions. A general method of measuring the internal pressure based on the Maxwell's equation of thermodynamics [16] is

$$P = T \left[ \frac{\partial p}{\partial T} \right]_v - \left[ \frac{\partial E}{\partial v} \right]_T \quad (5)$$

On the basis of statistical thermodynamics, expression for the determination of internal pressure by the use of free volume concept as given by

$$v_f = \frac{1}{V^2} \left[ \frac{bRT}{P + \left( \frac{\partial E}{\partial v} \right)_T} \right]^3 \quad (6)$$

As  $\left( \frac{\partial E}{\partial v} \right)_T$  is the internal pressure and neglecting P which is insignificantly small to  $\pi_i$ , the equation can be written as,

$$v_f = \frac{1}{V^2} \left[ \frac{bRT}{\pi_i} \right]^3 \quad (7)$$

The final equation for the evaluation of internal pressure can be obtained by combining and rearranging the equations (6) and (7)

$$\pi_i = bRT \left( \frac{K\eta}{U} \right)^{\frac{1}{2}} \left( \frac{\rho^{\frac{2}{3}}}{M^{\frac{7}{6}}} \right) \quad (8)$$

Where K is a constant, T the absolute temperature,  $\eta$ , the viscosity in  $\text{Nsm}^{-2}$ , U, the ultrasonic velocity in  $\text{ms}^{-1}$ ,  $\rho$ , the density in  $\text{kgm}^{-3}$  of the liquid.

## 5. Relaxation time ( $\tau$ )

Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and on impurities.

The dispersion of the ultrasonic velocity in binary mixture reveals information about the characteristic time of the relaxation process that causes dispersion. The relaxation time ( $\tau$ ) can be calculated from the relation.

$$\tau = \frac{4}{3} \beta \eta \quad (9)$$

## 6. Acoustic Impedance (Z)

The Specific acoustic impedance is given by

$$Z = U\rho \quad (10)$$

Where U and  $\rho$  are velocity and density of liquid respectively.

## 7. Gibb's Free Energy ( $\Delta G^*$ )

The relaxation time for a given transition is related to the activation free energy. The variation of  $\tau$  with temperature can be expressed in the form of Eyring salt process theory.

$$\frac{1}{\tau} = \frac{KT}{h} \exp\left(\frac{-\Delta G^*}{KT}\right) \quad (11)$$

The above equation can be rearranged as,

$$\Delta G^* = -KT \log\left(\frac{h}{KT\tau}\right) \quad (12)$$

Where K is the Boltzmann constant and h is plank's constant.

## 3. Experimental

### 1. Density Measurement

The density of pure liquids and mixtures are measured using a 10ml specific gravity bottle. The specific gravity bottle with the experimental liquid is immersed in a temperature controlled water bath. The densities of pure liquids thus obtained are found to be in good agreement with standard values. The measured density was measured using the formula,

$$\rho_2 = \frac{W_2}{W_1} \rho_1 \quad (13)$$

Where,

W1, is the weight of the distilled water.

W2, that of weight of the experimental liquid.

$\rho_1$ , is the density of water.

$\rho_2$ , that of the experimental liquid.

## 2. Viscosity measurement

The viscosity of the pure liquids and liquid mixtures are measured using an Ostwald's Viscometer calibrated with doubly distilled water. The Ostwald's Viscometer with the experimental liquid is immersed in a temperature controlled water bath. The time of flow was measured using a Racer stop watch with an accuracy of 0.1 sec. Viscosity was determined using the relation

$$\eta_2 = \eta_1 \frac{t_2 \rho_2}{t_1 \rho_1} \quad (14)$$

Where,

$\eta_1$ , is the Viscosity of water  
 $t_1$ , is the time of flow of water

$\rho_1$ , is the density of water.

$\eta_2$ , is the viscosity of the experimental liquid.  
 $t_2$ , is the time of flow of the experimental liquid.

$\rho_2$ , is the density of the experimental liquid.

## 3. Velocity Measurement

The velocity of ultrasonic waves in the liquid mixture have been measured using an ultrasonic interferometer (Mittal Enterprises, New Delhi) working at a fixed frequency of 2MHZ with a tolerance of  $\pm 0.005\%$ . The measuring cell is a specially designed double-walled vessel with provision for temperature constancy. The high frequency generator excites a quartz crystal fixed at the bottom of the measuring cell, at its resonant frequency. The capacity of the measuring cell is 12cc. A fine micrometer screw, with a least count of 0.01mm at the top of the cell, can be raised (or) lowered the reflector plate in the liquid through a known distance. The measuring cell is connected to the output terminals of the high frequency generator through a shielded cable. Ultrasonic waves, normal to quartz crystal, is reflected from the reflector plate. Stationary waves are formed in the region between reflector plate and the quartz crystal. The micrometer is slowly moved till a number of maximum readings (n) of the anode current is passed. The total distance moved by the micrometer is noted (d).

The wavelength of the ultrasonic waves in the liquid is  $\lambda = 2d/n$ . The velocity of ultrasonic waves in the liquid  $U = \lambda f$ . Where  $f$  is the frequency of the generator.

## 4. Results and Discussion

The experimental values of density viscosity, ultrasonic velocity for the three binary systems Methylmethacrylate + 2-Methoxy Ethanol, Methylmethacrylate + 2-Ethoxy Ethanol, Methylmethacrylate + 2-Butoxy Ethanol at 303k are given in the tables 1, 2, 3.

The parameters adiabatic compressibility ( $\beta_{ad}$ ), free length  $L_f$ , free volume ( $V_f$ ), acoustic impedance (Z), internal pressure  $\pi_i$ , relaxation time  $\tau$  at 303k are listed in tables 4,5,6,7,8,9.

**Table 1**  
**SYSTEM 1: Values of Density ( $\rho$ ), Viscosity ( $\eta$ ) and Velocity (U) of**  
**Methylmethacrylate + 2 Methoxy ethanol at 30<sup>0</sup>c.**

Mole Fraction		$\rho$ Kgm <sup>-3</sup>	$\eta \times 10^3$ Nsm <sup>-2</sup>	U ms <sup>-1</sup>
X <sub>1</sub>	X <sub>2</sub>			
0.1	0.9	879.5220	1.36473	1421
0.2	0.8	883.2290	1.25480	1408
0.3	0.7	885.6231	1.14795	1246
0.4	0.6	888.2246	0.8745	1245
0.5	0.5	890.8073	0.79932	1235
0.6	0.4	898.4056	0.7725	1069
0.7	0.3	901.5124	0.73033	1008
0.8	0.2	905.3490	0.71089	930
0.9	0.1	920.2837	0.6939	920

**Table 2**  
**SYSTEM 2: Values of Density ( $\rho$ ), Viscosity ( $\eta$ ) and Velocity (U) of**  
**Methylmethacrylate + 2 Ethoxy ethanol at 30<sup>0</sup>c.**

Mole Fraction		$\rho$ Kgm <sup>-3</sup>	$\eta \times 10^3$ Nsm <sup>-2</sup>	U ms <sup>-1</sup>
X <sub>1</sub>	X <sub>2</sub>			
0.1	0.9	898.7238	1.9041	1638
0.2	0.8	902.6166	1.8787	1500
0.3	0.7	904.0764	1.7296	1460
0.4	0.6	909.0546	1.2179	1360
0.5	0.5	910.2524	0.8962	1232
0.6	0.4	910.4957	0.8454	1080
0.7	0.3	910.6494	0.7831	1000
0.8	0.2	911.1133	0.7324	920
0.9	0.1	911.2817	0.7212	600

**Table 3**  
**SYSTEM 3: Values of Density ( $\rho$ ), Viscosity ( $\eta$ ) and Velocity (U) of**  
**Methylmethacrylate + 2 Butoxy ethanol at 30<sup>0</sup>c.**

Mole Fraction		$\rho$ Kgm <sup>-3</sup>	$\eta \times 10^3$ Nsm <sup>-2</sup>	U ms <sup>-1</sup>
X <sub>1</sub>	X <sub>2</sub>			
0.1	0.9	881.5619	2.7742	2246
0.2	0.8	883.3773	2.2923	1530
0.3	0.7	887.7419	1.8252	1498
0.4	0.6	889.6656	1.6632	1474
0.5	0.5	891.7056	1.3169	1440
0.6	0.4	896.2534	1.1728	1418
0.7	0.3	899.2665	0.8630	1230
0.8	0.2	904.2074	0.7882	990
0.9	0.1	909.6161	0.7312	680

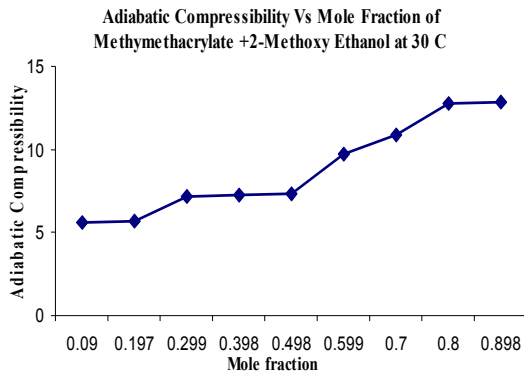
**Table 4**  
**SYSTEM 1: Values of Adiabatic compressibility ( $\beta$ ), Free Length ( $L_f$ ) and Free Volume ( $V_f$ ) of Methylmethacrylate + 2 Methoxy ethanol at 30<sup>0</sup>c.**

Mole Fraction		$\beta \times 10^{-10} \text{ m}^2/\text{N}$	$L_f \times 10^{-10} \text{ m}$	$V_f \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$
$X_1$	$X_2$			
0.090	0.900	5.6307	0.4735	0.8196
0.197	0.802	5.7112	0.4768	0.9755
0.299	0.700	7.1410	0.5432	0.9789
0.398	0.601	7.2633	0.5377	1.5220
0.498	0.501	7.3600	0.5413	1.5832
0.599	0.400	9.7402	0.6227	1.6407
0.700	0.299	10.9170	0.6592	1.6643
0.800	0.199	12.7707	0.7130	1.7937
0.898	0.101	12.8381	0.7149	1.8327

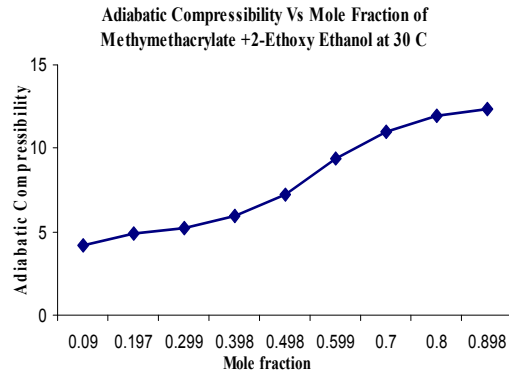
**Table 5**  
**SYSTEM 2: Values of Adiabatic compressibility ( $\beta$ ), Free Length ( $L_f$ ) and Free Volume ( $V_f$ ) of Methylmethacrylate + 2 Ethoxy ethanol at 30<sup>0</sup>c.**

Mole Fraction		$\beta \times 10^{-10} \text{ m}^2/\text{N}$	$L_f \times 10^{-10} \text{ m}$	$V_f \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$
$X_1$	$X_2$			
0.090	0.900	4.1471	0.4063	0.7117
0.197	0.802	4.9239	0.4427	0.7837
0.299	0.700	5.1890	0.4545	0.7861
0.398	0.601	5.9474	0.4866	1.2162
0.498	0.501	7.2379	0.5368	1.5583
0.599	0.400	9.4161	0.6122	1.6881
0.700	0.299	10.9876	0.6613	1.6987
0.800	0.199	11.9673	0.6903	1.7237
0.898	0.101	12.3682	0.7017	1.7683

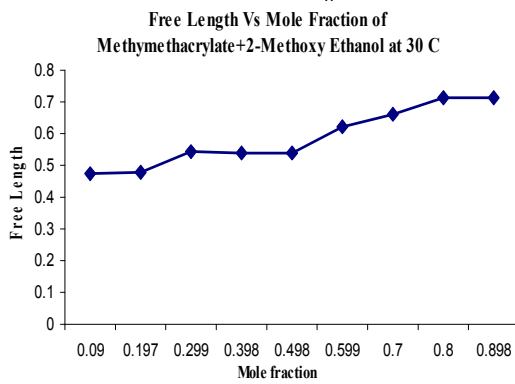




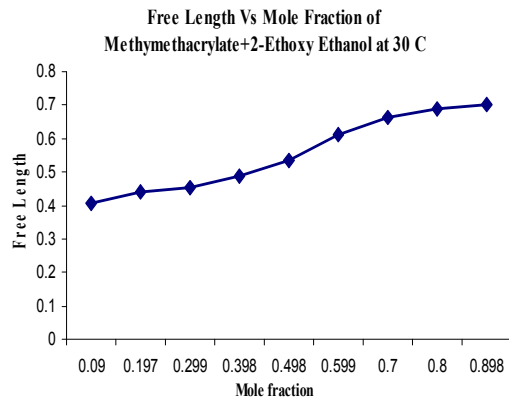
**Figure 1.** Adiabatic Compressibility Vs Mole Fraction of Methymethacrylate +2-Methoxy



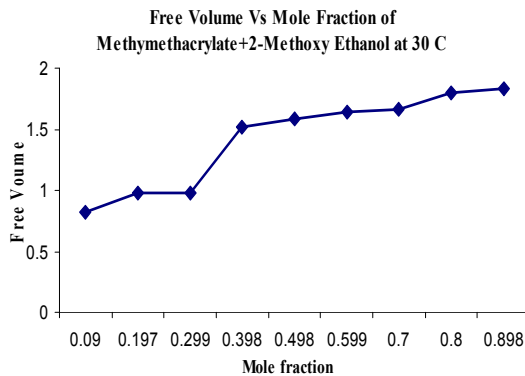
**Figure 4.** Adiabatic Compressibility Vs Mole Fraction of Methymethacrylate +2-Ethoxy



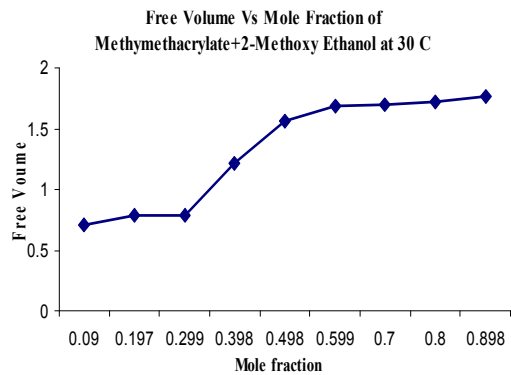
**Figure 2.** Free Length Vs Mole Fraction of Methymethacrylate +2-Methoxy Ethanol at



**Figure 5.** Free Length Vs Mole Fraction of Methymethacrylate +2-Ethoxy Ethanol at 30<sup>0</sup> C



**Figure 3.** Free Volume Vs Mole Fraction of Methymethacrylate +2-Methoxy Ethanol at 30<sup>0</sup> C



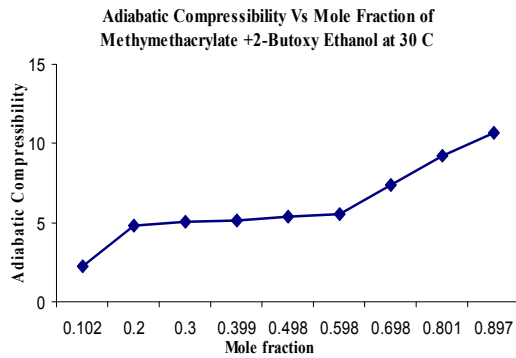
**Figure 6.** Free Volume Vs Mole Fraction of Methymethacrylate +2-Ethoxy Ethanol at 30<sup>0</sup> C

**Table 6**  
**SYSTEM 3: Values of Adiabatic compressibility ( $\beta$ ), Free Length ( $L_f$ ) and Free Volume ( $V_f$ ) of Methylmethacrylate + 2 Butoxy ethanol at 30<sup>o</sup>c.**

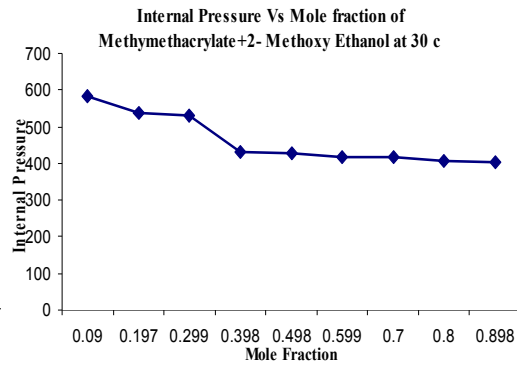
Mole Fraction		$\beta \times 10^{-10} \text{ m}^2/\text{N}$	$L_f \times 10^{-10} \text{ m}$	$V_f \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$
$X_1$	$X_2$			
0.102	0.897	2.2486	0.2992	1.0330
0.200	0.799	4.8358	0.4376	1.1053
0.300	0.699	5.0198	0.4470	1.3567
0.399	0.600	5.1734	0.4583	1.4724
0.498	0.501	5.4082	0.4640	1.5906
0.598	0.401	5.5490	0.4700	1.6703
0.698	0.301	7.3502	0.5409	1.7507
0.801	0.198	9.2436	0.6066	1.9372
0.897	0.102	10.6478	0.6510	2.0840

**Table 7**  
**SYSTEM 1: Values of Relaxation time ( $\tau$ ), Internal pressure ( $\pi_i$ ), Acoustic Impedance ( $Z$ ) and Gibb's Free Energy ( $\Delta G^*$ ) of Methylmethacrylate + 2 Methoxy ethanol at 30<sup>o</sup>c.**

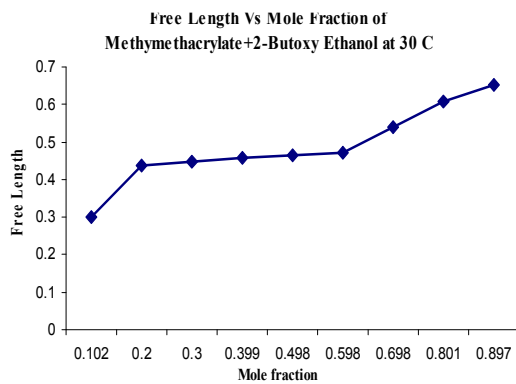
Mole Fraction		Internal Pressure $\pi_i \times 10^{-6} \text{ Pa}$	Relaxation time $\tau \times 10^{-12} \text{ S}$	Acoustic Impedance $Z \times 10^3 \text{ Kg}^{-1} \text{ m}^2 \text{ S}^{-1}$	Gibb's Free Energy $\Delta G^* \times 10^{-20} \text{ KJ mol}^{-1}$
$X_1$	$X_2$				
0.090	0.900	584.2	1.2074	124.91	0.8497
0.197	0.802	538.0	1.1848	124.25	0.8418
0.299	0.700	529.1	1.1132	110.58	0.8157
0.398	0.601	430.0	1.0603	110.34	0.7954
0.498	0.501	429.5	1.0220	110.01	0.7800
0.599	0.400	417.9	1.0007	96.89	0.7712
0.700	0.299	417.0	0.9525	90.87	0.7503
0.800	0.199	407.8	0.8447	84.66	0.7003
0.898	0.101	402.8	0.7821	84.17	0.6681



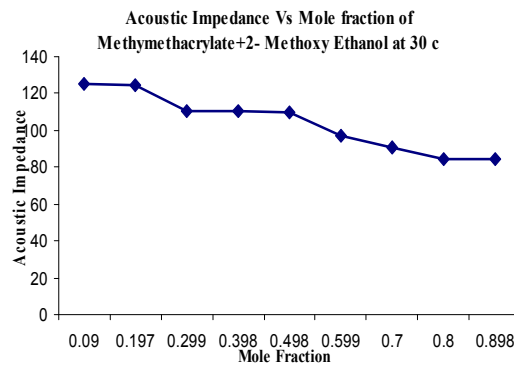
**Figure 7.** Adiabatic Compressibility Vs Mole Fraction of Methymethacrylate +2-Butoxy Ethanol at 30<sup>0</sup> C



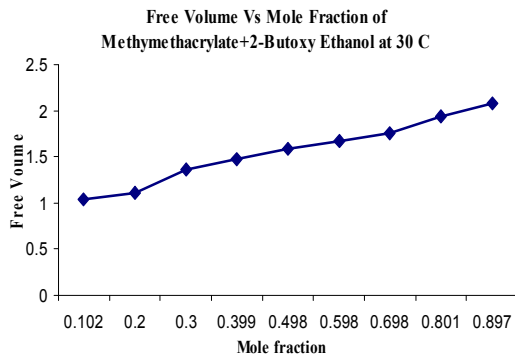
**Figure 10.** Internal Pressure Vs Mole Fraction of Methymethacrylate +2-Methoxy Ethanol at 30<sup>0</sup> C



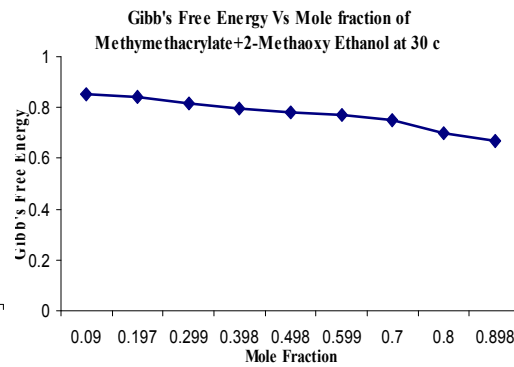
**Figure 8.** Free Length Vs Mole Fraction of Methymethacrylate +2-Butoxy Ethanol at 30<sup>0</sup> C



**Figure 11.** Acoustic Impedance Vs Mole Fraction of Methymethacrylate +2-Methoxy Ethanol at 30<sup>0</sup> C



**Figure 9.** Free Volume Vs Mole Fraction of Methymethacrylate +2-Butoxy Ethanol at 30<sup>0</sup> C



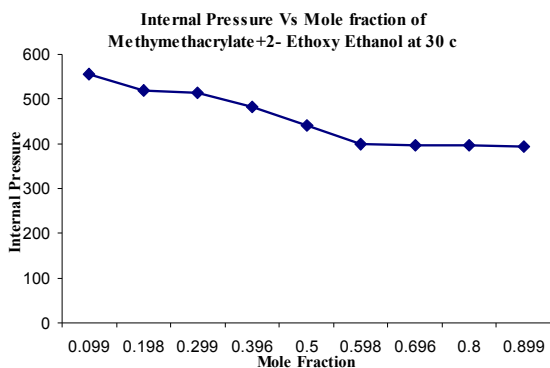
**Figure 12.** Gibb's free Energy Vs Mole Fraction of Methymethacrylate +2-Methoxy Ethanol at 30<sup>0</sup> C

**Table 8**  
**SYSTEM 2: Values of Relaxation time ( $\tau$ ), Internal pressure ( $\pi_i$ ), Acoustic Impedance (Z) and Gibb's Free Energy ( $\Delta G^*$ ) of Methylmethacrylate + 2 Ethoxy ethanol at 30<sup>o</sup>c.**

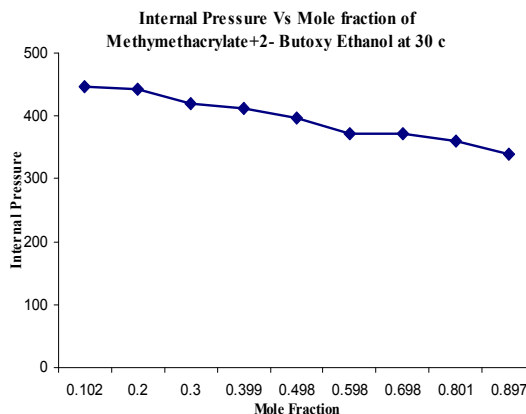
Mole Fraction		Internal Pressure $\pi_i \times 10^{-6}$ Pa	Relaxation time $\tau \times 10^{-12}$ S	Acoustic Impedance $Z \times 10^3 \text{ Kg}^{-1} \text{ m}^2 \text{ S}^{-1}$	Gibb's Free Energy $\Delta G^* \times 10^{-20} \text{ KJ mol}^{-1}$
$X_1$	$X_2$				
0.099	0.900	556.0	1.230	147.21	0.8575
0.198	0.801	519.0	1.119	135.39	0.8179
0.299	0.700	513.3	1.118	131.99	0.8175
0.396	0.603	482.9	1.116	123.63	0.8160
0.500	0.499	442.0	1.114	112.14	0.7945
0.598	0.401	399.1	1.058	98.33	0.7913
0.696	0.303	397.5	1.050	91.06	0.7551
0.800	0.199	396.5	0.963	83.82	0.7088
0.899	0.100	393.8	0.862	54.67	0.6898

**Table 9**  
**SYSTEM 3: Values of Relaxation time ( $\tau$ ), Internal pressure ( $\pi_i$ ), Acoustic Impedance (Z) and Gibb's Free Energy ( $\Delta G^*$ ) of Methylmethacrylate + 2 Butoxy ethanol at 30<sup>o</sup>c.**

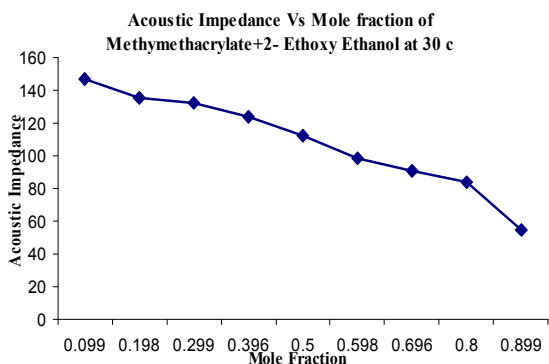
Mole Fraction		Internal Pressure $\pi_i \times 10^{-6}$ Pa	Relaxation time $\tau \times 10^{-12}$ S	Acoustic Impedance $Z \times 10^3 \text{ Kg}^{-1} \text{ m}^2 \text{ S}^{-1}$	Gibb's Free Energy $\Delta G^* \times 10^{-20} \text{ KJ mol}^{-1}$
$X_1$	$X_2$				
0.102	0.897	446.0	1.474	197.99	0.9332
0.200	0.799	441.8	1.218	135.15	0.8537
0.300	0.699	420.4	1.035	132.98	0.8272
0.399	0.600	411.1	0.9691	131.13	0.7853
0.498	0.501	397.2	0.9476	128.40	0.7578
0.598	0.401	371.0	0.865	127.08	0.7482
0.698	0.301	370.8	0.8436	110.60	0.7104
0.801	0.198	360.9	0.8296	89.51	0.6997
0.897	0.102	339.7	0.8193	61.85	0.6927



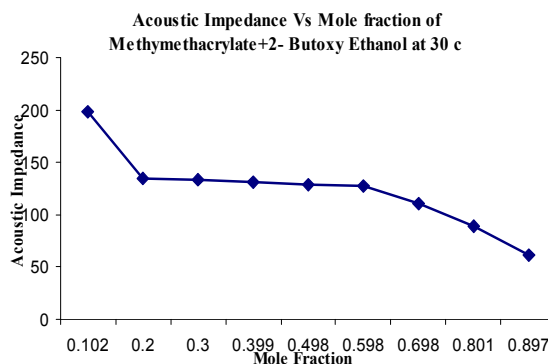
**Figure 13.** Internal Pressure Vs Mole Fraction of Methymethacrylate +2-Ethoxy Ethanol at 30<sup>0</sup> C



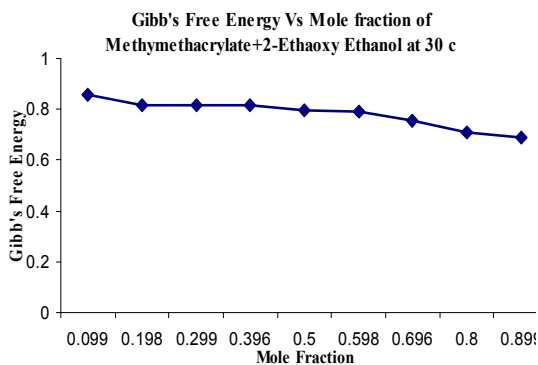
**Figure 16.** Internal Pressure Vs Mole Fraction of Methymethacrylate +2-Ethoxy Ethanol at 30<sup>0</sup> C



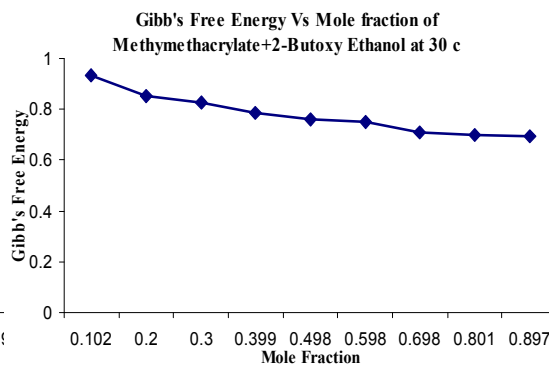
**Figure 14.** Acoustic Impedance Vs Mole Fraction of Methymethacrylate +2-Ethoxy Ethanol at 30<sup>0</sup> C



**Figure 17.** Acoustic Impedance Vs Mole Fraction of Methymethacrylate +2-Ethoxy Ethanol at 30<sup>0</sup> C



**Figure 15.** Gibb's free Energy Vs Mole Fraction of Methymethacrylate +2-Ethoxy Ethanol at 30<sup>0</sup> C



**Figure 18.** Gibb's free Energy Vs Mole Fraction of Methymethacrylate +2-Ethoxy Ethanol at 30<sup>0</sup> C

From the tables 1 to 3 it is noted that the density increases with increase in mole fraction for all the cases. Ultrasonic velocity and viscosity decreases with increase in mole fraction of the solute in all the systems.

The decrease in velocity is due to the increase in free length and adiabatic compressibility of the liquid mixtures. It is observed that for a given concentration as the number of CH group or chain length increases, the sound velocity increases. The adiabatic compressibility and free length increases with increase of mole fraction in all the systems. 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 liquid systems. The internal pressure decrease and free volume increases with increasing mole fraction. The internal pressure may give information regarding the nature and strength of forces existing between the molecules. The decrease in free volume shows that the strength of interaction decreases gradually with the increase in solute concentration. It represents that there is weak interaction between the solute and solvent molecules.

Acoustic impedance decreases with increase of mole fraction in all the three systems. The relaxation time ( $\tau$ ) decreases with increasing concentration for all the three systems. The dispersion of the ultrasonic velocity in the system should contain information about the characteristic time  $\tau$  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 [17] and in such a situation it is suggested that the molecules get rearranged due to co-operative process [18).

The Gibb's Free energy decreases with increasing mole fraction of all the systems. This may be due to the intermediate compound formation between binary liquids. It is observed generally free energy decrease favors the formation of products from reaction. This observation confirms the formation of hydrogen bonding in binary mixtures.

## 5. Conclusion

The computed acoustical parameters and their values point to the presence of specific molecular interaction in the mixtures. Hence it is concluded that the association in these mixtures is the result of Hydrogen bonding in Binary liquid mixtures.

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