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Ultrasonic Studies on Molecular Interactions in Ternary Liquid Mixtures at Different Temperatures

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ABSTRACT

The ultrasonic velocity, density, viscosity have been measured for ternary liquid mixtures containing 4-methyl anisole and 2-Propanol in n-hexane as solvent at 303K, 308K and 313K. The various acoustic parameters like adiabatic compressibility, free length, free volume, internal pressure, acoustic impedance, formation constant values have been calculated from the experimental data. In addition to that excess values of certain above parameters are also evaluated. These parameters are used to discuss the presence of significant molecular interaction between the components of ternary liquid mixtures.

Keywords: Ultrasonic velocity; Acoustic parameters; Molecular interaction; Excess values

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INTRODUCTION

The study of molecular interaction plays a vital role in characterizing physico-chemical behavior of liquid mixtures [1-3]. It has attracted the attention of many researchers and extensive investigations have been carried out by different techniques [4]. Though spectroscopic methods play a major part in 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. Variations in Ultrasonic velocity and related parameters like Adiabatic compressibility, Free length, Free volume, Internal pressure, etc. yield information regarding structural changes in solutions. The excess properties have been claimed to be an aid in the characterization of molecular interactions present in liquid mixtures. This is achieved through elevation of ideal quantities. In recent years considerable efforts have been given for evaluation of ideal and excess thermodynamic quantities of binary and ternary liquid mixtures [5].

In the present study the measurements on ultrasonic velocity, density, viscosity and their related excess thermodynamic parameters for 4 methyl anisole and 2-propanol with n-hexane system has been performed at 303K, 308K and 313K to investigate the molecular interactions between the liquid components. The n-hexane is a non-polar chain molecule, where vanderwaal's type interactions are present, while alcohols are polar and associate strongly through hydrogen bonding. In alcohol + n-hexane mixtures the alcohol molecules associate in inert hexane medium and form clusters.

THEORY AND CALCULATIONS

To prepare liquid mixtures of various concentrations the AR grade chemicals were purified and used. The ultrasonic velocity measurement were made using an ultrasonic interferometer (Mittal type: Model: F81) working at frequency

2MHz with accuracy of ±0.1ms^{-1}. The density and viscosity were measured using a Pycknometer and an Ostwald's viscometer with an accuracy of ±0.1kgm^{-3} and ± 0.001 Nsm^{-2} respectively, at various temperatures 303K, 308K, 313K.

I. Ultrasonic velocity (u): U = fλ ms^{-1} ----------1
Where **f**=Frequency of the Ultrasonic waves; **λ**=Wavelength.

II. Densities of the mixture: $\rho_2 = (w_2/w_1)\ \rho_1$ ----------2
Where $\mathbf{w_1}$ = weight of distilled water; $\mathbf{w_2}$ = weight of experimental liquid; $\boldsymbol{\rho_1}$ = Density of water; $\boldsymbol{\rho_2}$ = Density of experimental liquid.

III. Viscosity: $\eta_2=\eta_1(t_2/t_1)(\rho_2/\rho_1)$ ----------3
Using these measured data, the following parameters can be calculated.
1. Adiabatic Compressibility (k): K= (1/u^{2}ρ) kg^{-1} ms^{-2} ----------4
2. Free Length: L_f = (K/Uρ$^{1/2}$) m ----------5 Where **U** - Ultrasonic velocity of liquid; **ρ** - Density of liquid; **K** - Jacobson temperature **K= (93.875 + 0.345T) X 10^{-8}**
3. Free Volume (V_f): V_f = (M_{eff}U/Kη)$^{3/2}$ m^3 ----------6 Where**, E**ffective molecular weight $\mathbf{M_{eff}}$ = ($X_1M_1+X_2M_2+X_3M_3$), X and M are mole fraction and molecular weight of the individual component in the mixture respectively. **K**=4.28x10$^{9.}$
4. Internal Pressure (π_i): π_i= bRT (kη/U)$^{1/2}$ (ρ$^{2/3}$/M_{eff})$^{7/6}$ ----------7 Where **T** - Absolute temperature; **ρ**- Density, R is the gas constant.
5. Lenard Jones Potential (LJP): LJP = 6V_m/V_a ----------8 Where $\mathbf{V_m}$- the molar volume and $\mathbf{V_a}$ - the available volume
6. Acoustic Impedance (Z): Z =ρ.U kgm^{-2} s^{-1} ----------9
7. Formation constant K:
To calculate formation constant values of the charge transfer complexes, appreciable to weak complexes and in very dilute solutions.
The stability constant is calculated using the relation
K=Y/(b-y)^{2}dm^3 mol^{-1}----------10
Where, Y = [(a-k$^{1/2}$b)/k-k$^{1/2}$)]; k=x/y
X=difference between Ucal and Uobs at lower concentration 'a'.
y=difference between Ucal and Uobs at higher concentration 'b'.
8. Excess Parameters (A^E)
In order to study the non-ideality of the liquid mixtures, the difference between the values of the real mixture (A_{exp}) and those corresponding to an ideal mixture (A_{id}), namely the excess parameters (A^E) of some of the acoustic parameters, were computed using the equation
$A^E=A_{exp}-A_{id}$----------11
Where $A_{id} = \Sigma^n A_i X_i$, '$A_i$' is any parameter and '$X_i$' the mole fraction of liquid component i.

RESULTS AND DISCUSSION

Experimental values of density, viscosity, ultrasonic velocity for the ternary mixtures at different temperatures are presented in Table.1. The calculated values of different parameters are shown in the Tables 2 & 3. The excess values of the parameters are calculated and tabulated in Table 4 & 5. The relations between the parameters are shown on the figures 1 to12.

The interactions become weak with increase in temperature due to the thermal agitation of component molecules, which is also indicated by decrease in ultrasonic velocity values [6-8]. The variation of the ultrasonic velocity depends upon increase or decrease of intermolecular free length after mixing the components. According to Eyring Kincaid [9] model ultrasonic velocity should increase, if the inter molecular free length decreases and vice versa as a result of mixing of components. This trend is seen in this system also.

Table 1: Values of Ultrasonic velocity, Density and Viscosity of the system: 4 methyl anisole +2propanol + n-hexane

CONC (M)	Ultrasonic Velocity (U) ms^{-1}			Density ρ kg/m^3			Viscosity η $\times10^{-4}$ Nsm^{-2}		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
0.001	1056	1013.5	1008.4	639	637	632	3.504	3.359	3.199
0.002	1054.4	1017.4	1002.8	639	635	634	3.504	3.348	3.209
0.003	1051	1016	1006.4	638	636	633	3.499	3.353	3.204
0.004	1053	1018	1004.2	637	634	631	3.493	3.343	3.194
0.005	1055.7	1014.8	1006.8	638	635	631	3.499	3.348	3.194
0.006	1058	1014.4	1000.3	638	636	635	3.499	3.353	3.214
0.007	1044.9	1016.9	1006.9	636	634	632	3.488	3.343	3.199
0.008	1049.2	1018.4	1010.2	639	635	635	3.504	3.348	3.204
0.009	1052	1012.4	1013.7	640	634	633	3.509	3.343	3.204
0.01	1055.1	1013	1009.3	638	636	635	3.499	3.353	3.214

Table 2: Values of Adiabatic Compressibility (k), Free Length (L_f), Free Volume (V_f) & Internal pressure (π_i) of the system: 4 methyl anisole + 2-propanol + n-hexane at different temperatures

CONC (M)	Adiabatic Compressibility k $\times10^{-9}$ $kg\text{-}1ms^{-2}$			Free Length (L_f) $\times10^{-11}$m			Free Volume (Vf)$x10^{-7}$ m^3			Internal Pressure (πi)$X10^8$ Nm^{-2}		
	303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K
0.001	1.4	1.53	1.54	7.43	7.76	7.79	6.43	6.44	6.92	2.029	2.057	2.029
0.002	1.41	1.52	1.57	7.38	7.67	7.79	8.29	8.41	8.77	2.539	2.558	2.56
0.003	1.42	1.52	1.58	7.41	7.67	7.81	10.29	10.45	10.92	2.539	2.564	2.557
0.004	1.42	1.52	1.58	7.4	7.67	7.82	12.52	12.71	13.29	2.532	2.552	2.547
0.005	1.41	1.53	1.55	7.38	7.69	7.74	14.84	14.94	15.97	2.533	2.561	2.535
0.006	1.4	1.53	1.53	7.36	7.69	7.7	17.33	17.34	18.46	2.53	2.566	2.551
0.007	1.44	1.53	1.54	7.47	7.68	7.72	19.62	20.07	21.33	2.537	2.554	2.537
0.008	1.42	1.52	1.55	7.42	7.67	7.74	22.23	22.76	24	2.545	2.556	2.547
0.009	1.41	1.54	1.54	7.39	7.72	7.71	25.01	25.4	27.12	2.547	2.559	2.542
0.01	1.41	1.53	1.55	7.38	7.7	7.73	28.12	28.19	29.87	2.534	2.568	2.557

Table 3: Values of Acoustic Impedance, Lenard Jones Potential, Free Energy Activation, Molecular Interaction Parameter, and Formation Constant: 4 methyl anisole + 2-propanol + n-hexane at different temperatures

CONC (M)	Acoustic Impedance Z $\times10^5$ $Kgm^{-2}s^{-1}$			Lenard Jones Potential (LJP)			Free Energy Activation KJ/mol			Molecular Interaction Parameter λ ×10-2			Formation Constant		
	303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313k
0.001	6.75	6.46	6.41	4.647	3.368	3.382	3.91	4.15	4.41	-0.76	-1.27	-0.08	103	124.2	89.1
0.002	6.74	6.46	6.36	4.595	3.478	3.075	3.93	4.13	4.21	-1.06	-0.52	-2.21	76.7	83.3	65.1
0.003	6.71	6.46	6.34	4.486	3.438	3.037	3.95	4.14	4.22	-1.71	-0.8	-2.49	62.5	21.1	60.9
0.004	6.71	6.45	6.32	4.55	3.495	3.054	3.93	4.13	4.21	-1.34	-0.42	-2.38	49.3	40.8	49.1
0.005	6.74	6.44	6.39	4.637	3.405	3.327	3.92	4.14	4.16	-0.84	-1.06	-0.43	7.4	35.2	39.2
0.006	6.75	6.45	6.44	4.768	3.393	3.377	3.91	4.15	4.15	-0.42	-1.14	-0.09	35.6	24	28.1
0.007	6.65	6.45	6.41	4.294	3.464	3.371	3.98	4.13	4.15	-2.88	-0.67	-0.13	30.4	28.7	26.5
0.008	6.7	6.47	6.39	4.429	3.506	3.26	3.95	4.12	4.17	-2.08	-0.38	-0.93	27.8	27.1	19.5
0.009	6.73	6.42	6.42	4.518	3.338	3.374	3.93	4.16	4.15	-1.57	-1.56	-0.13	22.4	21	19.6
0.01	6.73	6.44	6.41	4.618	3.354	3.252	3.92	4.15	4.17	-0.99	-1.45	-1			

As the temperature increases the density and viscosity decreases. This may be due to more spacing between the molecules. The adiabatic compressibility, free length shows an inverse behavior compared to the ultrasonic velocity in the ternary mixtures. The structural arrangement of molecules results in increasing adiabatic compressibility thereby showing intermolecular interactions [10]. Acoustic impedance decreases with increase in temperature indicating weakening of molecular interaction. Alcohols are strongly self-associated liquids with a three dimensional network of hydrogen bonds and can be associated with any other group having some degree of polar attractions [11].

The only dominant interaction is dipole – dipole interaction between 4-methyl anisole and 2-propanol.
Formation constant:

System	Mean K Value
4 methyl anisole + 2-propanol + n-hexane at 303 K	46.1
4 methyl anisole + 2-propanol + n-hexane at 308 K	45
4 methyl anisole + 2-propanol + n-hexane at 313 K	44.1

The formation constant is a measure of strength of the interaction between the liquid components that comes together to form a complex. Donor–acceptor complex is formed between 4-Methyl anisole (donor) and 2-propanol (acceptor). As $–CH_3$ group (+I effect) is present in 4-methyl anisole л electrons are easily donated to form charge transfer complex with 2-propanol. In the present system the formation constant and the stability of the complex is more at 303 K. The interaction becomes weak with increase in temperature due to thermal agitation of liquid components.

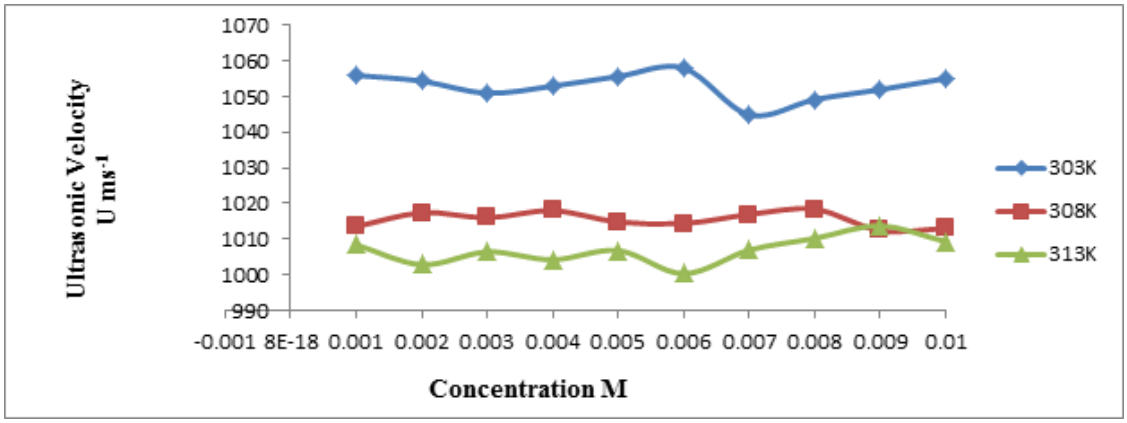

Figure 1: Variation of Ultrasonic Velocity Vs Concentration for system: 4 methyl anisole +2-propanol + n-hexane at different temperatures

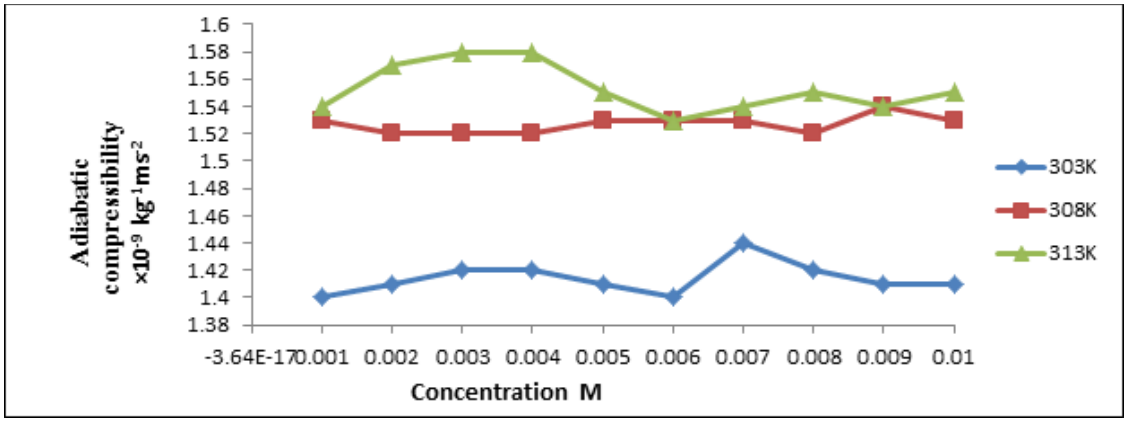

Figure 2: Variation of Adiabatic compressibility Vs Concentration for the system: 4 methyl anisole + 2-propanol + n-hexane at different temperatures

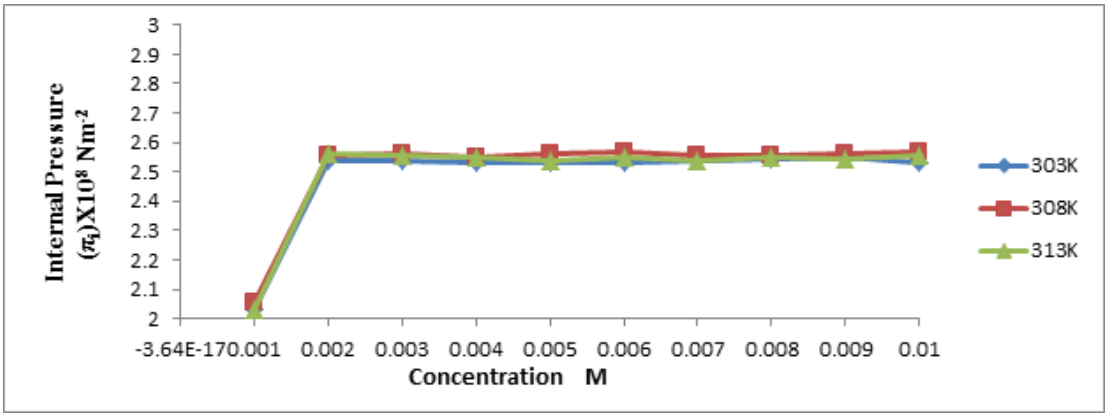

Figure 3: Variation of Internal pressure Vs Concentration for the system: 4 methyl anisole + 2-propanol + n-hexane at different temperatures

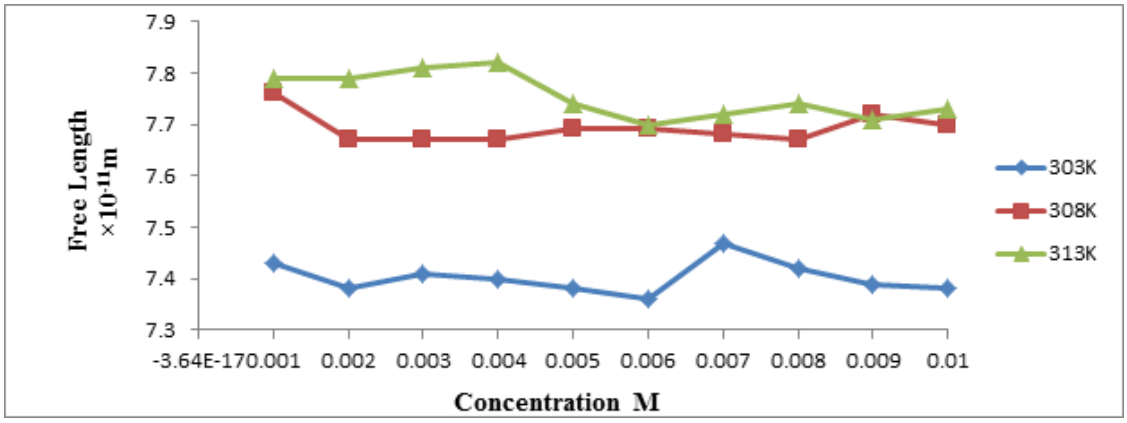

Figure 4: Variation of Free length Vs Concentration for the system: 4 methyl anisole +2-propanol + n-hexane at different temperatures

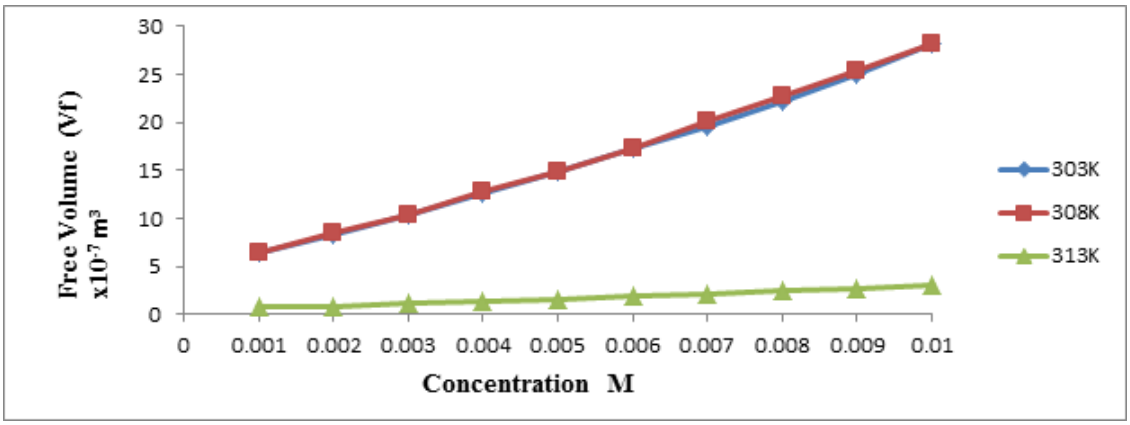

Figure 5: Variation of Free Volume Vs Concentration for the system: 4 methyl anisole + 2-propanol + n-hexane at different temperatures

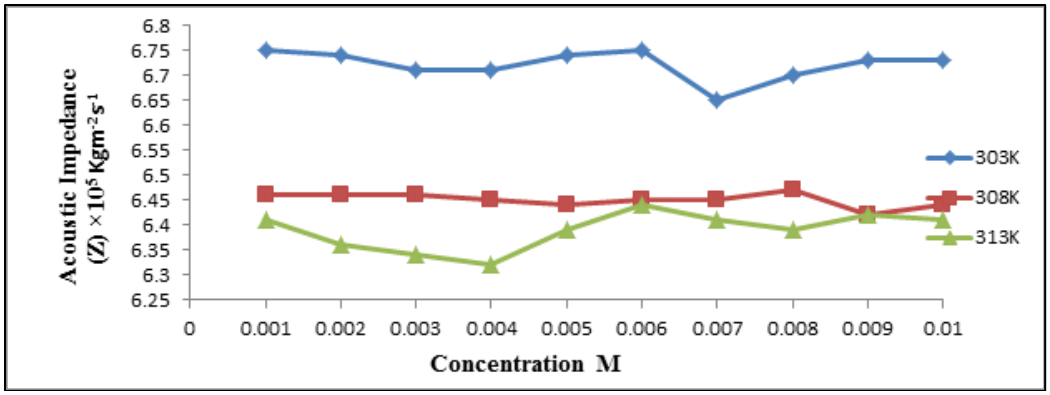

Figure 6: Variation of Acoustic Impedance Vs Concentration for the system: 4 methyl anisole + 2-propanol + n-hexane at different temperatures

Table 4: Values of Excess Ultrasonic velocity, Excess Adiabatic Compressibility and excess Free Length

S. No	Excess Ultrasonic velocity ms^{-1}			Excess Adiabatic Compressibility $\times10^{-10}kg^{-1}ms^{-2}$			Excess Free Length $\times10^{-10}$ m		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
1	-26.228	-32.03	-23.58	0.96	1.093	0.81	-6.52	-6.79	-6.9
2	-48.481	-51.86	-56.7	1.38	1.444	1.53	-6.31	-6.56	-6.65
3	-71.12	-75.37	-78.51	2	2.042	2.19	-6.1	-6.33	-6.42
4	-87.08	-94.01	-96.97	2.53	2.674	2.88	-5.91	-6.11	-6.21
5	-101.2	-116.53	-104.82	3.06	3.465	3.3	-5.74	-5.91	-6.02
6	-114.67	-135.05	-119.75	3.71	4.26	3.97	-5.57	-5.72	-5.84
7	-142.59	-149.58	-135.68	4.9	5.147	4.98	-5.4	-5.55	-5.66
8	-152.24	-164.12	-154.49	5.63	6.12	6.14	-5.26	-5.38	-5.49
9	-162.61	-185.24	-164.35	6.58	7.525	7.24	-5.12	-5.22	-5.34
10	-171.94	-198.93	-181.95	7.77	8.856	8.75	-4.99	-5.07	-5.19

Table 5: Values of Excess free volume, Excess internal pressure and excess acoustic impedance

S. No	Excess Free Volume $\times10^{-7}$ m^3			Excess Internal Pressure $\times10^{8}$ Nm^{-2}			Excess Acoustic Impedance $\times10^{6}$ $kgm^{-2}s^{-1}$		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
1	1.6305	1.5885	1.7413	0.306	0.329	0.316	-0.055	-0.053	-0.044
2	5.1029	5.1878	5.327	0.139	0.157	0.107	-0.101	-0.098	-0.093
3	7.4917	7.5891	7.8981	-0.153	-0.123	-0.128	-0.144	-0.14	-0.136
4	10.081	10.241	10.663	-0.433	-0.403	-0.415	-0.183	-0.18	-0.176
5	12.749	12.818	13.717	-0.687	-0.646	-0.686	-0.216	-0.218	-0.205
6	15.558	15.538	16.558	-0.929	-0.876	-0.911	-0.248	-0.252	-0.233
7	18.142	18.571	19.758	-1.15	-1.11	-1.15	-0.29	-0.285	-0.268
8	21.042	21.55	22.734	-1.35	-1.32	-1.36	-0.314	-0.314	-0.299
9	24.092	24.46	26.149	-1.55	-1.51	-1.56	-0.34	-0.347	-0.325
10	27.449	27.5	29.176	-1.75	-1.69	-1.74	-0.366	-0.372	-0.352

Excess parameters rather than the actual values are more useful to understand more about the nature of interaction between the components of liquid mixture. Rai et al suggested that the negative excess compressibility has been due to closed packed molecules and the positive excess values are due to weak interactions between the unlike molecules [12,13], hence supports the present investigation , in which positive adiabatic compressibility values are obtained due to the weak interactions .similar conclusions were also arrived by Debey et al [14] . Positive deviations of excess free volume are an indication of the existence of weak interaction between the components [15]. Negative excess internal pressure values in this system also support the presence of interaction.

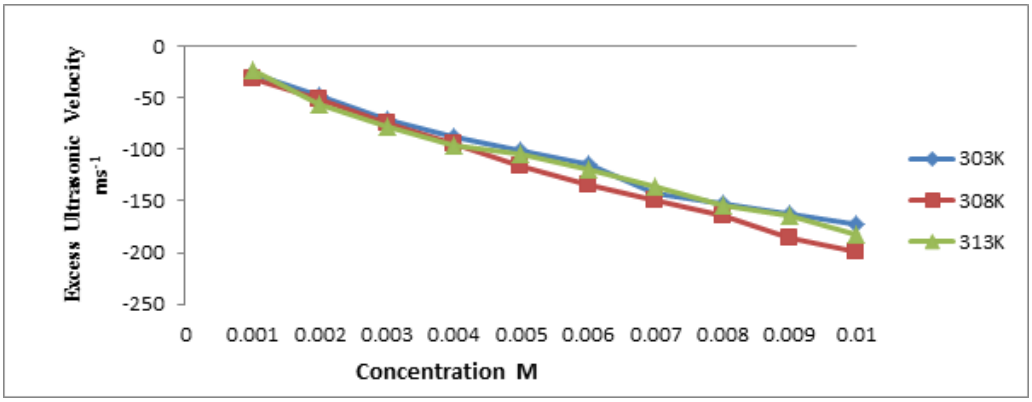

Figure 7: Variation Excess Ultrasonic Velocity of Vs Concentration for the system: 4 methyl anisole + 2-propanol + n-hexane at different temperatures

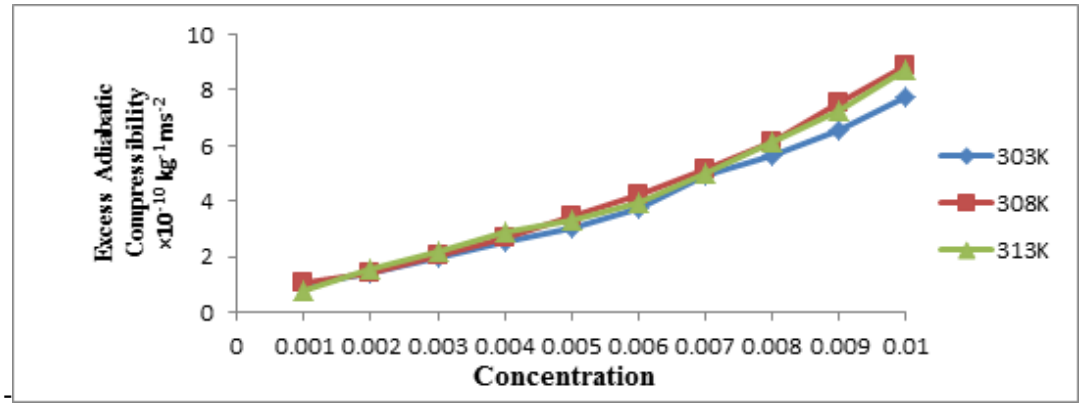

Figure 8: Variation of Excess Adiabatic Compressibility Vs Concentration for the system: 4 methyl anisole + 2-propanol + n-hexane at different temperatures

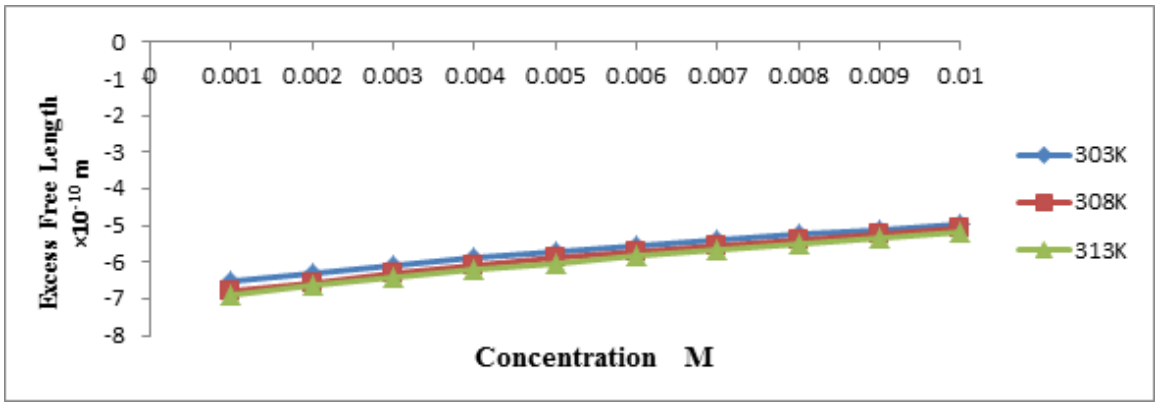

Figure 9: Variation of Excess Free Length Vs Concentration for the system: 4 methyl anisole + 2-propanol + n-hexane at different temperatures

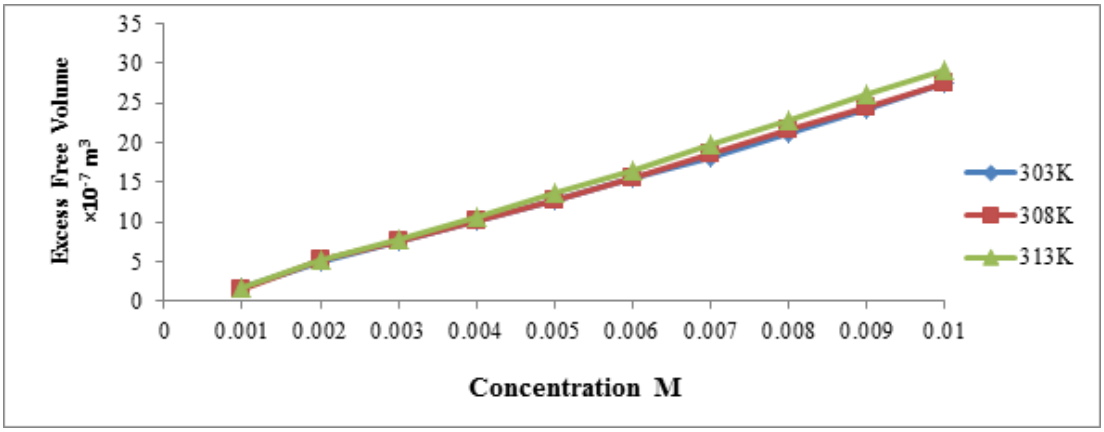

Figure 10: Variation of Excess Free Volume Vs Concentration for the system: 4 methyl anisole + 2-propanol + n-hexane at different temperatures

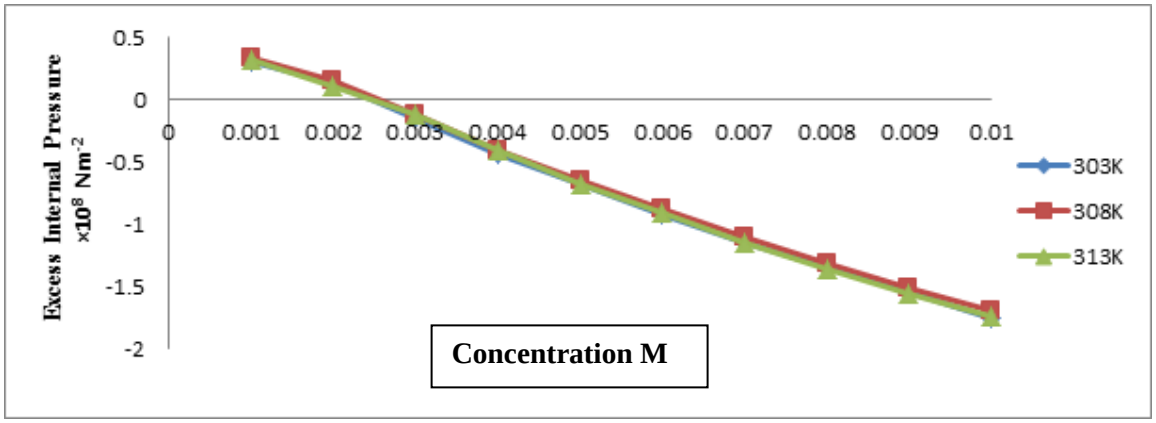

Figure 11: Variation of Excess Internal Pressure vs Concentration for the system: 4 methyl anisole + 2-propanol + n-hexane at different temperatures

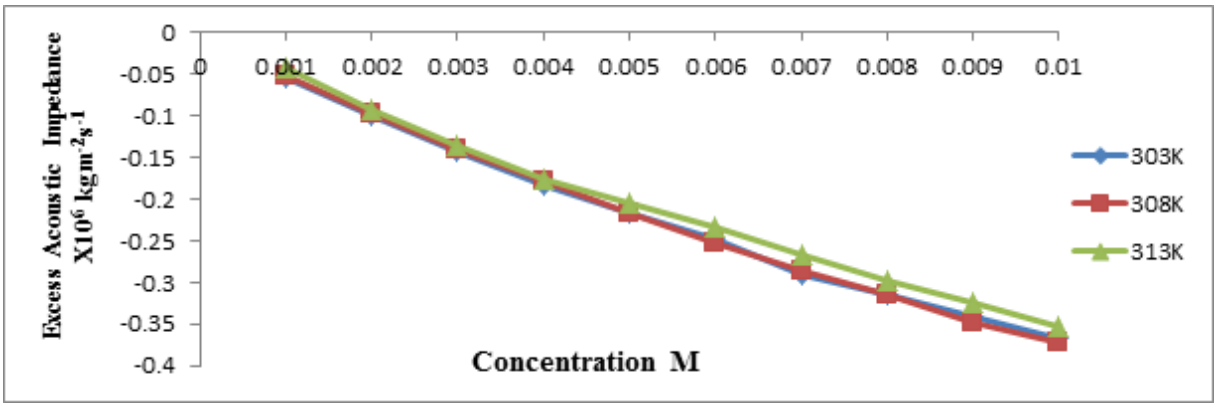

Figure 12: Variation of Excess Acoustic Impedance Vs Concentration for the system: 4 methyl anisole + 2-propanol + n-hexane at different temperatures

CONCLUSION

Variation of acoustic parameters derived from ultrasonic velocity, density, viscosity at different temperatures reveals the existence of molecular interactions in the ternary liquid mixture under study. The molecular interactions present in the chosen ternary mixture are dipole –dipole interaction between 4-methyl anisole and 2-propanol. Hydrogen bonding occurs between H atom of -OH group present in 2-propanol and O atom of 4-methyl anisole. It also forms the donor acceptor complex between them .The methyl group present in 4-methyl anisole enhance the electron donating capacity. The molecular interaction and stability of the complex is more at low temperature (303K). As the temperature increases interaction becomes weak, due to the thermal agitation of the liquid components.

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