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STUDY OF THERMOACOUSTICAL PARAMETERS OF BINARY LIQUID MIXTURES OF METHYL BENZOATE WITH 1-NONANOL AT DIFFERENT TEMPERATURES

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ABSTRACT

The ultrasonic velocity (U), the density (ρ) and viscosity (η) of binary liquid mixtures of Methyl Benzoate with 1-Nonanol have been measured at different temperatures 303.15K, 308.15K, 313.15K and 318.15K over the entire range of composition. From the measured data of ultrasonic velocity, density and viscosity, acoustic parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time (τ) and acoustic impedance (Z) have been estimated using standard relations. The variation of adiabatic compressibility (β), free length (L_f), free volume (V_f) internal pressure (π_i), relaxation time (τ) and acoustic impedance (Z) with concentration and temperature have been studied. Acoustic parameters provide important information in understanding the solute-solvent interaction in a polymer solution.

***Keywords*: Adiabatic Compressibility, Free Length , Free Volume, Internal Pressure, Relaxation Time**

I. INTRODUCTION

Ultrasonic investigations of liquid mixtures are of considerable importance in understanding intermolecular interactions between the component molecules and find applications in several industrial and technological processes [1-2]. The variation of ultrasonic velocity and other ultrasonic parameters of binary liquid mixtures have been studied by many researchers and they have shed light upon structural changes associated with liquid mixtures of weakly or strongly interacting compounds [3-8]. The study of molecular association in binary mixtures having alcohol as one of the component is of particular interest, since alcohols are strongly self-associated liquids having a three dimensional network of hydrogen bonds and can be associated with any other group having same degree of polar attractions [9-11]. But a systematic study with primary fatty alcohols in binary systems has been scarcely reported.

Methyl Benzoate is an ester, reacts with acids to liberate heat along with alcohols and acids. Methyl Benzoate is used in perfumery and also used as pesticide to attract insects. 1-Nonanol is a straight chain fatty alcohol with 9 carbon atoms. The primary use of 1-Nonanol is in the manufacture of artificial lemon oil , perfumery and flavors.

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Therefore in order to have a clear understanding of the intermolecular interactions between the component molecules, a thorough study on the binary liquid mixtures (Methyl Benzoate +1-Nonanol) using ultrasonic velocity data has been performed at temperatures 303.15K, 308.15K, 313.15K and 318.15K.

In the present study several acoustic parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time (τ) and acoustic impedance (Z) of a binary system Methyl Benzoate + 1- Nonanol have been reported using the experimental values of density, viscosity and ultrasonic velocity of the binary liquid mixtures at temperatures 303.15K, 308.15K, 313.15K and 318.15K.

II MATERIALS AND METHODS

2.1 Materials and Liquid Mixtures

The liquid mixtures of various concentrations in mole fraction were prepared by taking AR grade chemicals (obtained from SDFCL chemicals, Mumbai) Methyl Benzoate + 1- Nonanol (>99%). All the liquids used were further purified by standard procedure [12]. The mixtures were preserved in well-stoppered conical flasks. After the thorough mixing of the liquids, the flasks were left undisturbed to allow them to attain thermal equilibrium. In all the mixtures the mole fractions of 1^{st} compound Methyl Benzoate has been increased from 0 to1.

2.2 Apparatus and Procedure

The ultrasonic velocities were measured by using single crystal ultrasonic pulse echo interferometer (Mittal enterprises, India; Model: F-80X). It consists of a high frequency generator and a measuring cell. The measurements of ultrasonic velocities were made at a fixed frequency of 3MHz. The temperature was controlled by circulating water around the liquid cell from thermostatically controlled constant temperature water bath. The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of ± 0.5%. Weights were measured with an electronic balance (Shimadzu AUY220, Japan) capable of measuring up to 0.1mg. An average of 4-5 measurements was taken for each sample. From the experimentally measured vales of ultrasonic velocity (U), density (ρ) and viscosity (η) various acoustic parameters are calculated using the following relations [13-16] and discussed in this investigation.

III. THEORY AND CALCULATIONS

Adiabatic compressibility has been calculated from the speed of sound (U) and density (ρ) of the medium using the equation as:

$$\beta=1/(U^2 \rho) \qquad (1)$$

Intermolecular free length (L_f) has been determined using the standard relation as:

$$L_f = K_r\sqrt{\beta} \qquad (2)$$

Where K_r is a temperature dependant constant known as Jacobson's constant. The relation for free volume in terms of ultrasonic velocity (U) and viscosity (η) of the liquid as:

$$V_f = (M_{eff}\, U/\eta K)^{3/2} \qquad (3)$$

Where M_{eff} is the effective molecular weight ($M_{eff} = \Sigma m_i x_i$ in which m_i and x_i are the molecular weight and mole fraction of the individual components respectively). K is a temperature independent constant which is equal to $4.28x10^9$ for all liquids.

On the basis of statistical thermodynamics, Suryanarayana [17] derived an expression for determination of internal pressure by the use of free volume concept as:

$$\Pi_i = bRT(K\eta/U)^{1/2} (\rho^{2/3}/M_{eff}^{7/6}) \quad (4)$$

Where b stands for cubic packing factor which is assumed to be 2 for liquids and K is a constant, T is absolute temperature, η is the viscosity in Nsm^{-2}, U is the ultrasonic velocity in ms^{-1}, ρ is the density in kg m^{-3}, M_{eff} is the effective molecular weight and R is universal gas constant.

Relaxation time (τ) can be calculated using viscosity and adiabatic compressibility as:

$$\tau = (3/4)\eta\beta \quad (5)$$

The acoustic impedance is the parameter related to elastic properties of the medium and calculated by using the expression

$$Z = \rho U \quad (6)$$

where ρ is the density and U is the ultrasonic velocity.

IV. RESULTS AND DISCUSSION

The experimentally determined values of density (ρ), viscosity (η), and ultrasonic velocity (U) at 303.15K for pure components of the system Methyl Benzoate +1- Nonanol are listed in Table 1. The same values for the binary liquid mixture Methyl Benzoate +1-Nonanol at temperatures 303.15K, 308.15K, 313.15K and 318.15K are presented in Table 2.

From these observed values various acoustic parameters like adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time (τ) and acoustic impedance (Z) at temperatures 303.15K, 308.15K, 313.15K and 318.15K have been evaluated and is presented in Table 3 and Table 4.

From Table 2 it was observed that the ultrasonic velocity, density decreases with increasing mole fraction of 1-Nonanol while the viscosity increases. This may be due to association of a very strong dipole – induced dipole interaction between the component molecules. However the ultrasonic velocity, density, viscosity decreases in all the cases as temperature increases. The same result was obtained by A.N.Kannappan et al [18] and M.Umadevi et al [19].

Here with increase of temperature , due to thermal agitation of component molecules the interaction becomes weak and this is indicated by decrease in ultrasonic velocity values in the present investigation.

Table 3, Table 4 and Figs. 1-6 show the variation of adiabatic compressibility, free length, free volume, internal pressure, relaxation time and acoustic impedance with temperature and concentration respectively. From Table 3 and Figs. 1 & 2, it is observed that adiabatic compressibility and free length increase with increase in temperature and decrease with increase in concentration of Methyl Benzoate. The decrease in adiabatic compressibility indicates the enhancement of the bond strength at this concentration. From Table 3 and Fig. 3, it is also observed that the values of free volume increase with increase in temperature and it also increase with increase in concentration of Methyl Benzoate.

It is seen from Table 4 and Figs. 4 and 5 that internal pressure (π_i) and relaxation time (τ) decrease with increase in concentration of Methyl Benzoate. This is similar to the change found in viscosity, showing that viscous forces play a dominant role in the relaxation process. The variation of acoustic impedance with temperature and concentration is shown in Table 4 and Fig. 6. It is observed that the acoustic impedance decreases with increase in temperature and it increases with increase in concentration. This is in agreement with requirement as both ultrasonic velocity and density increase with increase in concentration of the solute and also effective due to solute-solvent interactions.

Table 1: The values of density (ρ), viscosity (η) and velocity (U) of pure liquids at 303.15K

Liquids	Density ρ (kg/m^3)	Viscosity η ($x10^{-3}Nsm^{-2}$)	Velocity U (m/s)
Methyl Benzoate	1087.5	0.1747	1404
1- Nonanol	816.45	0.9204	1348.42

Table 2: Density (ρ), viscosity (η) and ultrasonic velocity (U) for the binary mixtures of Methyl Benzoate +1- Nonanol at temperatures 303.15K, 308.15K, 313.15K and 318.15K

	T=303.15K			T=308.15K		
X_1	ρ (kg/m^3)	η($10^{-3}Nsm^{-2}$)	U (m/s)	ρ (kg/m^3)	η$x10^{-3}$(Nsm^{-2})	U (m/s)
0.0000	816.4560	0.00092038	1348.42	815.2730	0.00092038	1348.42
0.1355	841.7720	0.00086993	1353.33	840.8780	0.00086993	1353.33
0.2608	879.0790	0.00083774	1357.89	878.0570	0.00083774	1357.89
0.3769	893.2230	0.00075119	1361.05	892.2940	0.00075119	1361.05
0.4848	943.4450	0.00070199	1368.00	941.9680	0.00070199	1368.00
0.5853	947.7490	0.00064005	1370.00	946.6800	0.00064005	1370.00
0.6792	957.7940	0.00060604	1376.66	956.8190	0.00060604	1376.66
0.7671	997.9710	0.00053576	1380.00	996.7630	0.00053576	1380.00
0.8495	1016.8290	0.00037745	1392.63	1015.9160	0.00037745	1392.63
0.9270	1035.1750	0.00036864	1401.17	1034.1470	0.00036864	1401.17
1.0000	1087.5000	0.00017468	1404.00	1085.9000	0.00017468	1404.00
	T=313.15K			T=318.15K		
X_1	ρ (kg/m^3)	η($x10^{-3}Nsm^{-2}$)	U (m/s)	ρ (kg/m^3)	η($x10^{-3}Nsm^{-2}$)	U (m/s)
0.0000	813.7690	0.00077071	1338.00	812.3240	0.0007654	1329.47
0.1355	839.6500	0.00070755	1340.00	838.2710	0.0006876	1330.00
0.2608	876.4770	0.00064915	1340.00	874.8420	0.0006448	1332.30
0.3769	890.7980	0.0005981	1341.70	889.0410	0.0005832	1333.40
0.4848	940.3100	0.00055291	1343.33	938.4830	0.0005522	1334.11
0.5853	945.1180	0.00054232	1344.70	943.5910	0.0005428	1336.66
0.6792	954.8360	0.0005061	1346.66	952.5800	0.0005033	1338.00
0.7671	995.2430	0.00046202	1348.42	993.3400	0.0004253	1342.10

0.8495	1014.4750	0.00031356	1353.33	1012.8510	0.0003123	1343.33
0.9270	1032.6840	0.0003166	1360.80	1030.9320	0.0003115	1344.70
1.0000	1084.1000	0.00013131	1367.36	1083.8000	0.0001279	1348.42

Table 3: Adiabatic compressibility (β), free length (L_f) and free volume (V_f) of Methyl Benzoate and 1-Nonanal at temperatures 303.15K, 308.15K, 313.15K and 318.15K

	Adiabatic compressibility				Free length				Free volume			
	β (x $10^{-11}m^2/N$)				L_f (A°)				V_f (x$10^{-7}m^3$ mol^{-1})			
X_1	303.15K	308.15K	313.15K	318.15K	303.15K	308.15K	313.15K	318.15K	303.15K	308.15K	313.15K	318.15K
0.0000	67.3623	68.3105	68.6415	69.6488	0.0163	0.0165	0.0167	0.0169	3.4697	3.9227	4.4756	4.4793
0.1355	64.8632	65.5769	66.3273	67.4392	0.0160	0.0162	0.0164	0.0166	3.7532	4.3676	5.0414	5.2033
0.2608	61.6940	62.4899	63.5404	64.3971	0.0156	0.0158	0.0160	0.0163	3.9494	4.8870	5.6760	5.6845
0.3769	60.4355	61.1906	62.3605	63.2641	0.0154	0.0156	0.0159	0.0169	4.6213	5.4884	6.3664	6.5506
0.4848	56.6384	57.7357	58.9337	59.8674	0.0149	0.0152	0.0154	0.0157	5.1069	5.9285	7.1092	7.0505
0.5853	56.2167	57.1109	58.5145	59.3163	0.0149	0.0151	0.0154	0.0156	5.8278	6.4440	7.2659	7.1909
0.6792	55.0902	56.0925	57.7504	58.6390	0.0147	0.0150	0.0153	0.0155	6.3192	7.1925	8.0115	8.0001
0.7671	52.6167	53.3122	55.2612	55.8898	0.0144	0.0146	0.0150	0.0151	7.5717	8.2883	9.1322	10.2689
0.8495	50.7085	51.9384	53.8209	54.7128	0.0141	0.0144	0.0148	0.0150	12.8866	14.2879	16.3036	16.2237
0.9270	49.2045	50.7761	52.2930	53.6438	0.0139	0.0142	0.0145	0.0148	13.3821	14.6188	16.0922	16.1978
1.0000	46.6484	48.1237	49.3361	50.7458	0.0135	0.0139	0.0141	0.0144	40.8833	48.0391	60.2870	61.4210

Table 4: Internal pressure (π_i), relaxation time (τ) and acoustical impedance (Z) of Methyl Benzoate and 1-Nonanol at temperatures 303.15K, 308.15K, 313.15K and 318.15K

	Internal pressure				Relaxation time				Acoustical impedance			
	π_i (x10^6 N/m^2)				τ (x10^{-12} sec)				Z (x10^4 kg $m^{-2}sec^{-1}$)			
X_1	303.15K	308.15K	313.15K	318.15K	303.15K	308.15K	313.15K	318.15K	303.15K	308.15K	313.15K	318.15K
0.0000	227.84	222.10	215.73	218.86	0.8267	0.7676	0.7054	0.7108	110.09	109.25	108.88	108.00
0.1355	227.67	219.87	212.79	213.69	0.7524	0.6841	0.6257	0.6183	113.92	113.24	112.51	111.49
0.2608	231.50	219.02	211.49	214.49	0.6891	0.6021	0.5500	0.5536	119.37	118.54	117.45	116.56
0.3769	223.02	213.92	206.67	207.71	0.6053	0.5434	0.4973	0.4919	121.57	120.76	119.52	118.54
0.4848	224.66	217.06	207.38	211.00	0.5301	0.4850	0.4345	0.4408	129.06	127.73	126.31	125.20
0.5853	216.47	212.81	207.38	211.19	0.4798	0.4519	0.4231	0.4293	129.84	128.75	127.09	126.13
0.6792	212.97	207.20	202.85	205.86	0.4452	0.4123	0.3897	0.3935	131.86	130.61	128.58	127.46
0.7671	206.79	203.79	200.31	195.46	0.3759	0.3564	0.3404	0.3169	137.72	136.74	134.20	133.32
0.8495	175.94	172.69	167.78	170.56	0.2552	0.2412	0.2250	0.2278	141.61	139.86	137.29	136.06
0.9270	176.37	173.95	171.05	173.20	0.2418	0.2317	0.2207	0.2228	145.05	142.71	140.53	138.63
1.0000	125.97	121.23	114.09	115.17	0.1086	0.0992	0.0864	0.0865	152.69	150.22	148.24	146.14

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Fig. 1: Variation of Adiabatic compressibility with Mole fraction of Methyl Benzoate at temperatures 303.15K, 308.15K, 313.15K and 318.15K

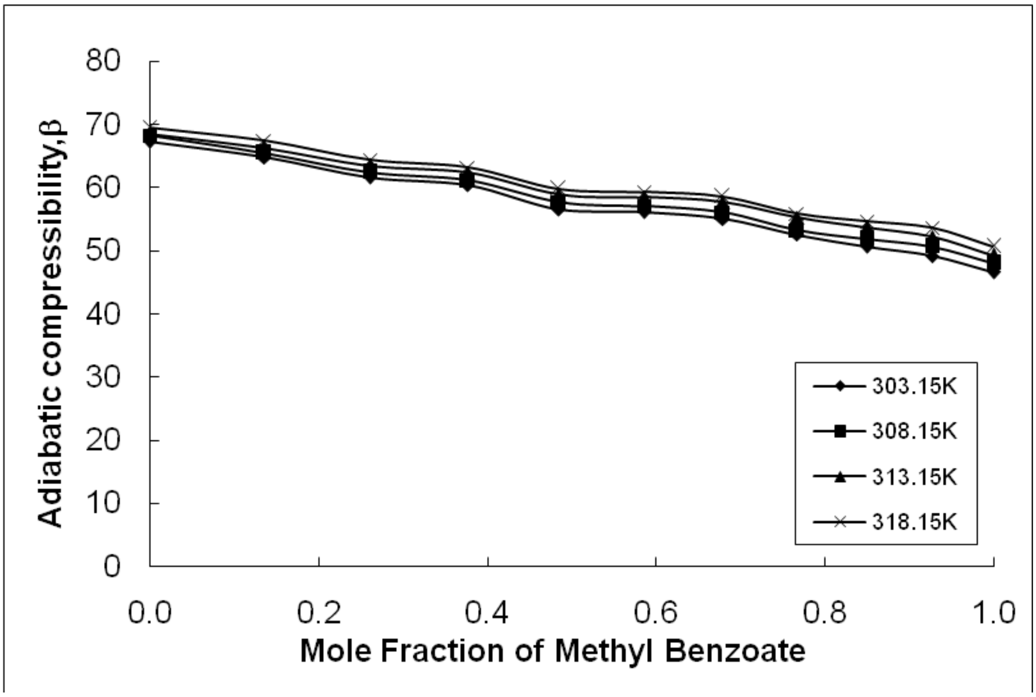

Fig. 2: Variation of Free length with Mole fraction of Methyl Benzoate at temperatures 303.15K, 308.15K, 313.15K and 318.15K

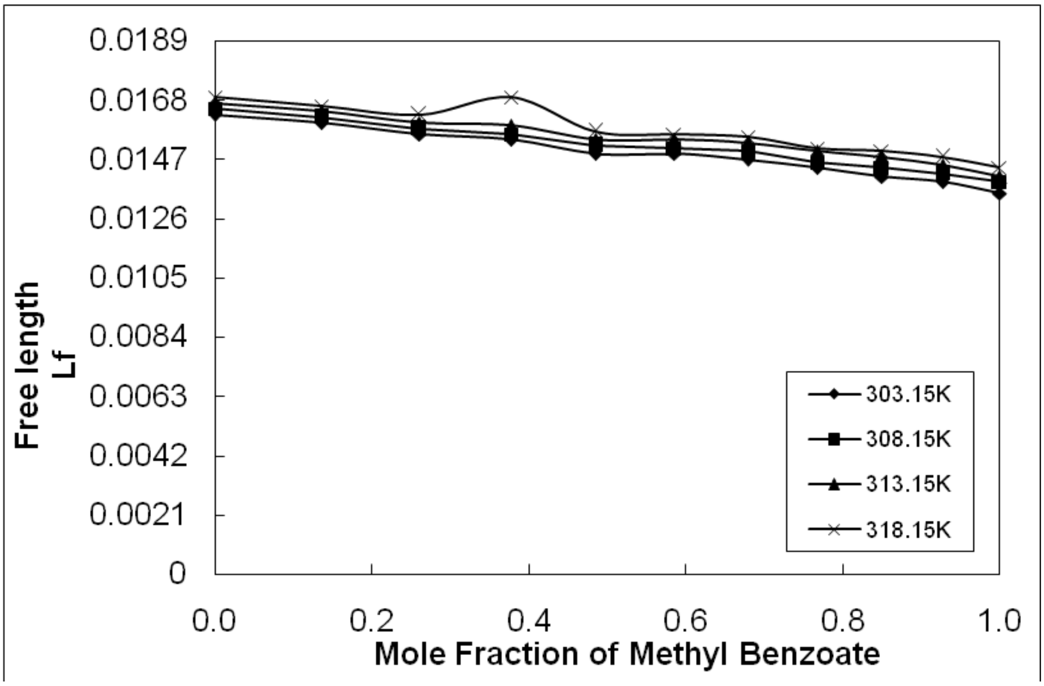

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Fig. 3: Variation of Free volume with Mole fraction of Methyl Benzoate at temperatures 303.15K, 308.15K, 313.15K and 318.15K

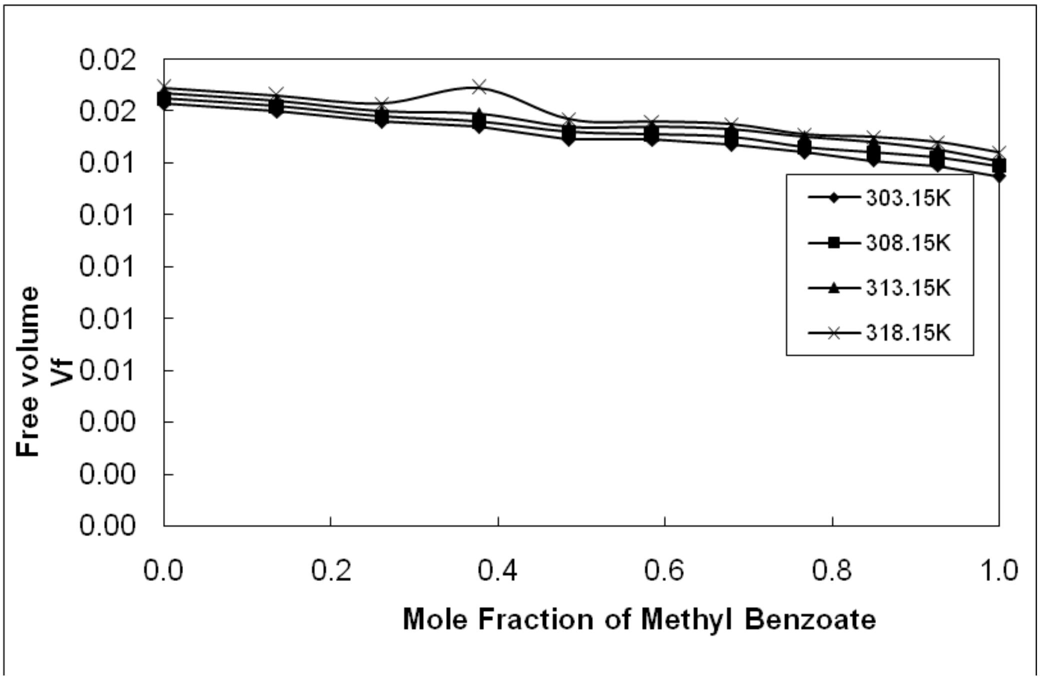


Fig. 4: Variation of Internal Pressure with Mole fraction of Methyl Benzoate at temperatures 303.15K, 308.15K, 313.15K and 318.15K

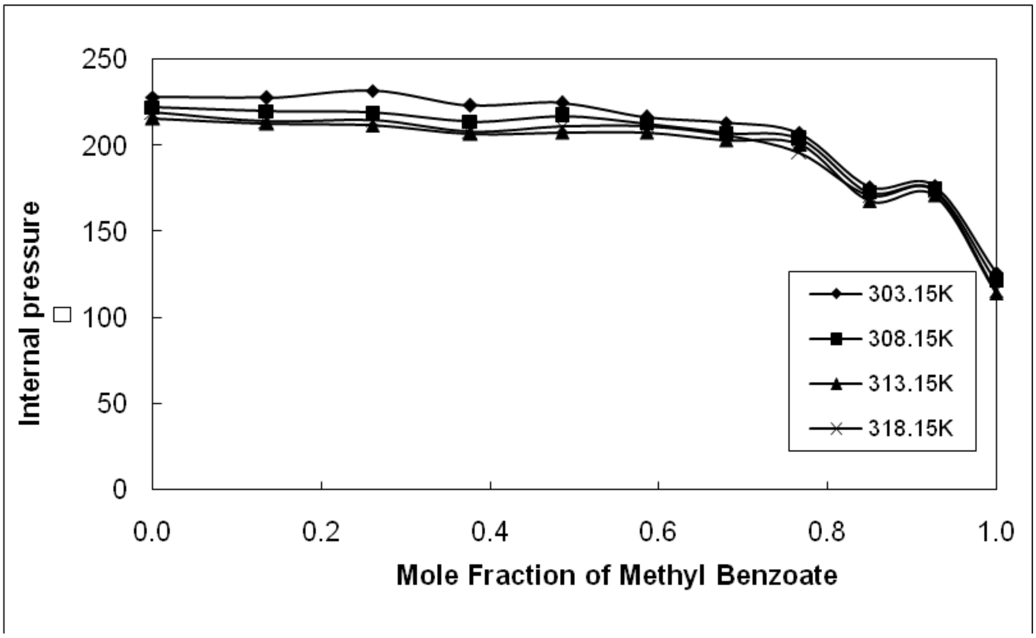


Fig. 5: Variation of Relaxation time with Mole fraction of Methyl Benzoate at temperatures 303.15K, 308.15K, 313.15K and 318.15K

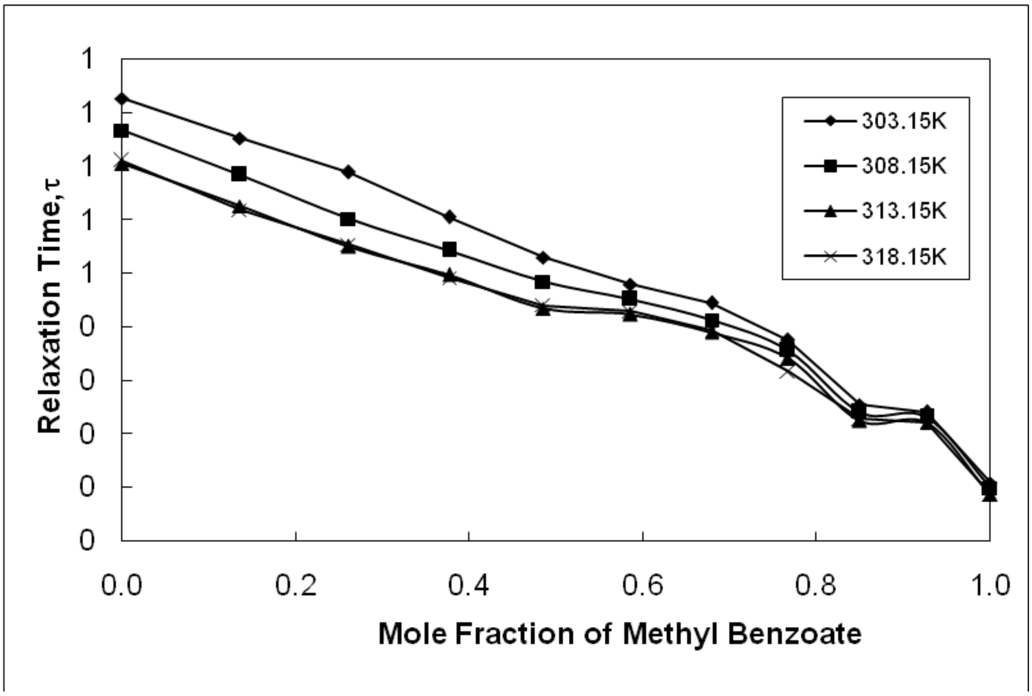
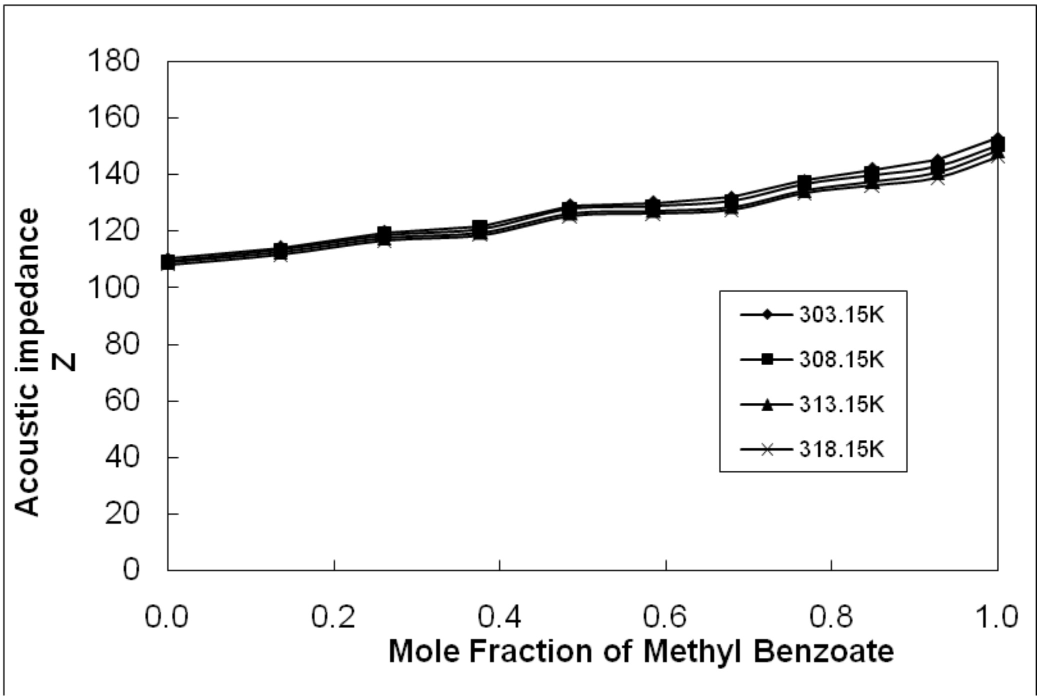


Fig. 6: Variation of Acoustic Impedance with Mole fraction of Methyl Benzoate at temperatures 303.15K, 308.15K, 313.15K and 318.15K



V. CONCLUSION

From the observed experimental values of density, viscosity and ultrasonic velocity and related acoustical parameters values for the binary liquid mixtures of Methyl Benzoate and 1- Nonanol system at temperatures 303.15K, 308.15K, 313.15K and 318.15K, it is clear that there exists a strong intermolecular association between the component molecules of the liquid mixtures. In the present system when the temperature increases, the interaction between the component molecules decreases.

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