International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064

Ultrasonic Study of Molecular Interaction in Binary Liquid Mixtures at 303 K, 308 K and 313 K

S. Rajavelu[1]

[1]Department of Physics, PSNA College of Engineering and Technology,
Dindigul- 624 622, Tamilnadu, India

Abstract: ***The ultrasonic velocity (U), the density (ρ) and viscosity (η) of methyl benzoate with 1-Octanol have been measured at 303K, 308K, and 313K 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), 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), 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, internal pressure, relaxation time, acoustic impedance, binary liquid mixture.

1. Introduction

Ultrasonic investigations of liquid mixtures consisting of polar and non polar components are of considerable importance in understanding intermolecular interactions between the component molecules [1-3]. 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 [4-6]. 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 [7-10]. 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. Octanol is a straight chain fatty alcohol with 8 carbon atoms. 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-octanol) using ultrasonic velocity data has been performed at temperatures 303K, 308K and 313K. In the present study several acoustic parameters such as adiabatic compressibility (β), free length (Lf), internal pressure (πi), relaxation time (τ) and acoustic impedance (Z) of a binary system methyl benzoate +1-octanol have been reported using the experimental values of density, viscosity and ultrasonic velocity of the binary liquid mixtures at temperatures 303K, 308K and 313K.

2. Experiment

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-octanol (>99%). 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 1st compound Methyl Benzoate has been increased from 0 to1.

2.2 Apparatus and Procedure

The ultrasonic velocities were measured by using a single crystal ultrasonic pulse echo interferometer (Pico enterprises, India; Model: BL-02). The measurements of ultrasonic velocities were made at a fixed frequency of 2MHz. 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 0.1 mg. From the experimentally measured values of ultrasonic velocity (U), density (ρ) and viscosity (η), various acoustic parameters are calculated using the following relations [11, 12].

2.3 Theory and Calculations

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

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

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

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

Where K_r is a temperature dependant constant known as Jacobson's constant.

On the basis of statistical thermodynamics, Suryanarayana [13] derived an expression for determination of internal pressure by the use of free volume concept as:

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

K is a temperature independent constant which is equal to 4.28×10^9 for all liquids. Where b stands for cubic packing factor which is assumed to be 2 for liquids, T is a 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:

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

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

$$Z = \rho U \quad (5)$$

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

3. Results and Discussion

The experimentally determined values of density (ρ), viscosity (η), and ultrasonic velocity (U) at 303K for pure components of the system Methyl Benzoate +1-Octanol are listed in Table-1. The same values for the binary liquid mixture Methyl Benzoate +1-Octanol at temperatures 303K, 308K and 313K are presented in table-2.

Table 1: The values of density (ρ), viscosity (η) and velocity (U) of pure liquids at 303K

Liquids	*Density ρ* (kg/m^3)	*Viscosity η* $(x10^{-3}Nsm^{-2})$	*Velocity U* *(m/s)*
Methyl Benzoate	1087.5	0.1739	1400
1-Octanol	803.03	0.6310	1370

Table 2: Density (ρ), viscosity (η) and ultrasonic velocity (U) for the binary mixtures of Methyl Benzoate +1-Octanol at temperatures 303K, 308K and 313K

X_1	T= 303 K			T= 308K			T= 313 K		
	ρ (kg/m^3)	η $(10^{-3}Nsm^{-2})$	U (m/s)	ρ (kg/m^3)	η $(10^{-3}Nsm^{-2})$	U (m/s)	ρ (kg/m^3)	η $(10^{-3}Nsm^{-2})$	U (m/s)
0.0000	803.03	0.6306	1365.00	801.60	0.6171	1326.31	800.00	0.5890	1303.33
0.1258	836.40	0.4667	1370.52	835.00	0.4380	1329.47	833.40	0.3781	1306.66
0.2446	859.20	0.4344	1371.80	857.30	0.3969	1333.33	854.80	0.3680	1312.94
0.3570	902.50	0.2949	1376.84	900.10	0.2737	1343.33	897.80	0.2471	1320.00
0.4634	908.90	0.2793	1380.00	905.90	0.2484	1348.42	904.00	0.2372	1332.63
0.5643	938.00	0.2567	1383.52	935.50	0.2361	1351.76	933.80	0.2134	1335.78
0.6602	986.00	0.2237	1387.05	983.80	0.2071	1354.66	981.80	0.1893	1335.78
0.7514	986.30	0.2057	1390.00	984.00	0.1811	1357.89	982.10	0.1653	1338.94
0.8382	1011.80	0.1914	1396.66	1010.40	0.1764	1369.41	1008.30	0.1622	1346.66
0.9210	1059.10	0.1515	1400.00	1056.00	0.1396	1373.68	1054.80	0.1284	1354.73
1.0000	1087.50	0.1739	1400.00	1085.90	0.1546	1376.84	1084.10	0.1313	1370.36

Table 3: Adiabatic compressibility (β) and free length (L_f) Methyl Benzoate and 1-Octanol at temperatures 303K, 308K and 313K

X_1	*Adiabatic compressibility* β $(x\ 10^{-11}m^2/N)$			*Free length* L_f(A°)		
0.0000	66.8348	70.9173	73.587	0.0162	0.0168	0.0173
0.1258	63.6525	67.7574	70.2783	0.0158	0.0164	0.0169
0.2446	61.8478	65.6133	67.865	0.0156	0.0162	0.0166
0.3570	58.4502	61.5664	63.9253	0.0152	0.0157	0.0161
0.4634	57.7731	60.7113	62.2891	0.0151	0.0156	0.0159
0.5643	55.6963	58.5002	60.0173	0.0148	0.0153	0.0156
0.6602	52.7156	55.3902	57.083	0.0144	0.0149	0.0152
0.7514	52.4761	55.1157	56.7966	0.0144	0.0148	0.0152
0.8382	50.6669	52.7764	54.6883	0.0141	0.0145	0.0149
0.9210	48.1734	50.1841	51.6564	0.0138	0.0141	0.0145
1.0000	46.6484	48.5784	49.3361	0.0135	0.0139	0.0141

Table 4: Internal pressure (πi), relaxation time (τ) and acoustical impedance (Z) of Methyl Benzoate and 1- Octanol at temperatures 303, 308K and 313K

X_1	*Internal pressure* π_i $(x10^6\ N/m^2)$			*Relaxation time* τ $(x10^{-12}\ sec)$			*Acoustical impedance* Z $(x10^4\ kg\ m^{-2}sec^{-1})$		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
0.0000	208.87	212.82	212.86	0.5620	0.5835	0.5779	109.61	106.32	104.27
0.1258	183.04	182.80	173.88	0.3961	0.3957	0.3543	114.63	111.01	108.90
0.2446	178.57	175.73	172.97	0.3582	0.3472	0.3330	117.87	114.31	112.23
0.3570	150.88	149.32	145.20	0.2298	0.2247	0.2106	124.26	120.91	118.51
0.4634	146.54	141.80	141.44	0.2152	0.2011	0.1970	125.43	122.15	120.47
0.5643	142.53	140.33	136.21	0.1906	0.1842	0.1707	129.77	126.46	124.74
0.6602	136.70	135.09	132.01	0.1572	0.1529	0.1441	136.76	133.27	131.15
0.7514	130.38	125.62	122.65	0.1439	0.1331	0.1252	137.10	133.62	131.50
0.8382	127.03	125.09	122.76	0.1293	0.1241	0.1183	141.31	138.37	135.78
0.9210	115.88	113.94	111.73	0.0973	0.0934	0.0884	148.27	145.06	142.90
1.0000	125.97	121.51	114.09	0.1086	0.1001	0.0864	152.69	149.51	148.24

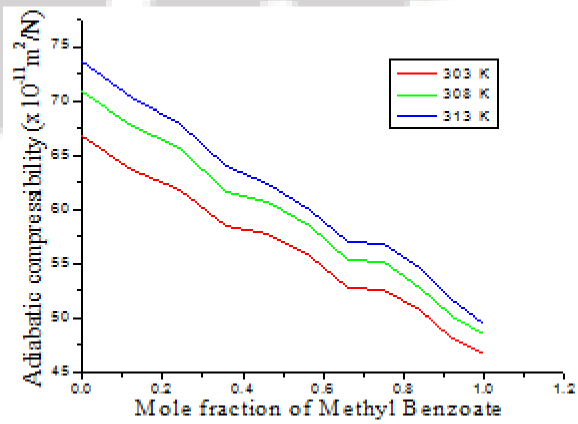

Figure 1: Variation of Adiabatic compressibility with Mole fraction of Methyl Benzoate at temperatures 303K, 308K and

313 K

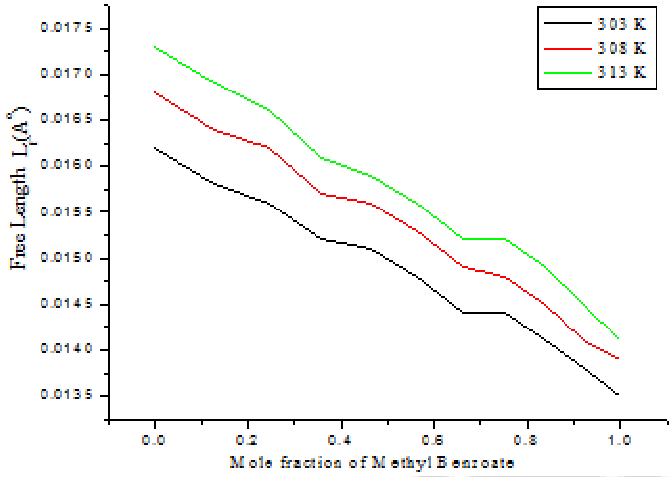

Figure 2: Variation of Free Length with Mole fraction of Methyl Benzoate at temperatures 303K, 308K and 313 K

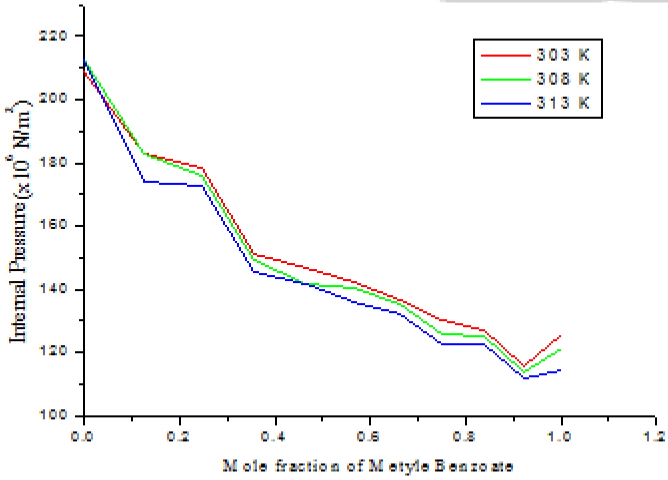

Figure 3: Variation of Internal Pressure with Mole fraction of Methyl Benzoate at temperatures 303K, 308K and 313 K

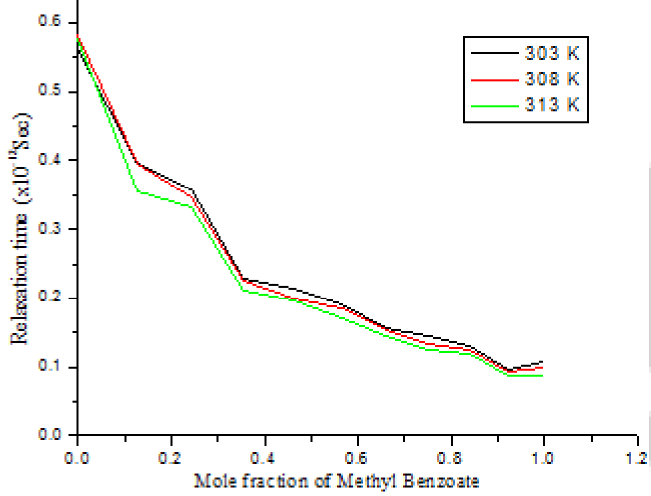

Figure- 4: Variation of Relaxation Time with Mole fraction of Methyl Benzoate at temperatures 303K, 308K and 313 K

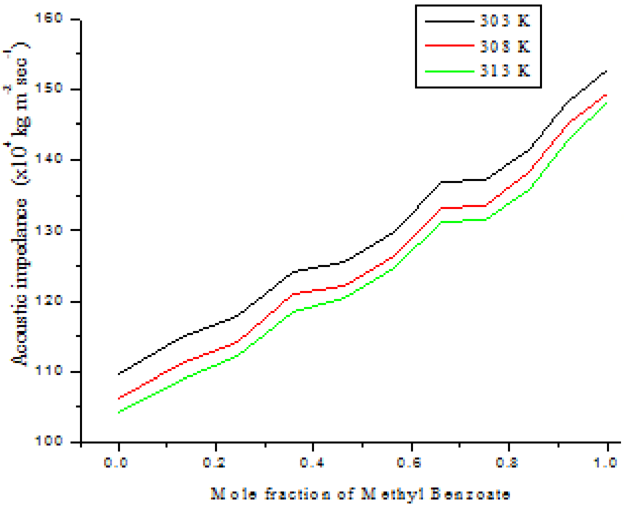

Figure 5: Variation of Acoustic impedance with Mole fraction of Methyl Benzoate at temperatures 303K, 308K and 313 K

From these observed values various acoustic parameters like adiabatic compressibility (β), free length (L_f), internal pressure (π_i), relaxation time (τ) and acoustic impedance (Z) at temperatures 303K, 308K and 313K have been evaluated and are presented in table-3 and table-4.

The variation of β, L_f, π_i, τ and Z with mole fraction of Methyl Benzoate at different temperatures are shown in figures-1-5.

From table-2, it was observed that the ultrasonic velocity and density decrease with increasing mole fraction of Octanol 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 S.Thirumaran et al [14] and M.Umadevi et al [15].

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, 4 and figures-1-5 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 figures-1 and 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.

It is seen from table-4 and figures-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 figure-6. It is observed 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.

4. 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-octanol system at temperatures 303K, 308K and 313K. We can understand 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.

References

[1] Srinivasalu, U. and Ramachandra Naidu, P., Ind. Pure & Appl. Phys, **29** 576 (1991)

[2] Ali A., Hyder S., Nain A.K.,Studies on molecular interactions in binary liquid mixtures by viscosity and ultrasonic velocity measurements at 303.15K, *Journal of Molecular Liquids*, **79**, (1999)

[3] Bhatt S.C., Semwal H.K., Lingwal V. and Semwal B.S., Acoustical parameters of some molecular liquids, *J. Acous. Soc. India*., **28**, 293-296 **(2000)**

[4] Ali A.A., Nain A.K. and Hyder S., Study of intermolecular interaction in binary liquid mixtures through ultrasonic speed measurement, *Journal of Pure and Applied Ultrasonics*, **23**, 73-79 (2001)

[5] Anuradha S., Prema S. and Rajagopal K., Ultrasonic studies on molecular interactions in binary mixtures of acetonitrile with carbonyl molecules, *Journal of Pure and Applied Ultrasonics*, **27,** 49-54 **(2005)**

[6] Palaniappan L. and Thiyagarajan R., Effect of aniline in methanol + benzene mixture – An ultrasonic study, *Ind. J. Chem.*, **47B**, 1906-1909 (2008)

[7] Tadkalkar A., Pawar P. and Bichile G.K., Studies of acoustic and thermodynamic properties of citric acid in double distilled water at different temperatures, *J. Chem. Pharm. Res*., **3(3)**, 165-168(2011)

[8] Ramteke J.N., Ultrasonic study of molecular interaction in binary liquid mixture containing α – picolin in ethanol at 301.15K and 305.15K, Advances in Applied Science Research, 3(3), 1832-1835 (2012)

[9] Bhatia S.C., Bhatia R. and Dubey G.P., Thermo-physical and sonochemical behavior of binary mixtures of hehxan-1-ol with halohydrocarbons at 303.15K, *Journal of Molecular Liquids*, 1**52**, 39-52 (2010)

[10] Sri devi, U., Samatha, K., and Viswanatha Sarma, A., J.Pure Appl Ultrason., 26 1 (2004)

[11] Bhatnagar D., Joshi D., Gupta R., Kumar Y., Kumar A. and Jain C.L., Studies on thermo acoustic parameters in binary liquid mixtures of MIBK with 1-propanol,1-butanol and 1- pentanol at 303.15K-A new approach by direct measurement of acoustic impedance, *Research Journal of Chemical Sciences*, **1(5)**, 6-13(2011)

[12] Nath G., Sahu S. and Paikaray R., Study of acoustical parameters of binary mixtures of a non-polar liquid at different frequencies, *Indian Journal of Physics*, **83(4)**, 429-436 (2009)

[13] Suryanarayana C.V., The liquid state-a new outlook, *J. Acoust. Soc. India*, **5**, 11-15 (1997)

[14] Thirumaran S. and Earnest Jayakumar J., Ultrasonic study of n– alkanols in toluene with nitrobenzene, *Indian Journal of Pure & Applied Physics*, **47**, 265-272 (2009)

[15] Umadevi M. and Kesavasamy R., Molecular interaction studies on ester with cyclohexane in alcohol at 303, 308, 313K, *International Journal of Chemical, Environmental and Pharmaceutical Research*, **3**, 72-82 (2012)