Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2015, 7(2):160-167
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Studies of molecular interaction in the binary mixture of chloroform and methanol by using ultrasonic technique

Kirandeep Kaur and Kailash C. Juglan*

Department of Physics, Lovely Professional University, Punjab, India

---

ABSTRACT

Ultrasonic velocity, density and viscosity of binary liquid mixtures of chloroform and methanol has been measured using ultrasonic interferometer, 30 ml gravity bottle and Oswald's viscometer respectively at frequency 2MHz and constant temperature of 295K. Experimental values then obtained are used for determining various thermo acoustical parameters like adiabatic compressibility, acoustic impedance, intermolecular free length, relaxation time, ultrasonic attenuation, effective molar weight, free volume, available volume, molar volume, Wada's constant, Rao's constant, Vander Waal's constant, internal pressure, Gibb's free energy and enthalpy. Graphs are plotted of each parameter against mole fraction. The linear variation in most of the acoustical parameters showed that there is no complex formation in the mixture. The weak interaction between the molecules of the binary mixture is founded.

Keywords: Ultrasonic velocity, molecular interaction, acoustical parameters.

INTRODUCTION

The propagation of ultrasonic waves in a substance has become a fundamental test to investigate its properties [1]. The important and fundamental role of the molecular details of the solvent species to determine the specific interactions have shown by many researchers, which are responsible for macroscopic thermodynamic and other related properties in non-electrolyte solutions [2, 3]. In the chemical process industries, materials are normally handled in fluid form and, as a consequence, their physical, chemical and transport properties assume importance [4, 5]. Ultrasonic technique offers a rapid non-destructive methods for characterizing material [6]. The ultrasonic velocity in a liquid is fundamentally related to the binding forces between atoms or molecules and has been successfully employed in the field of interactions and structural aspect studies, for characterizing the physico-chemical behavior of liquid mixtures [7-9].

The ultrasonic velocity along with density and viscosity furnish wealth of information about the interaction between ions, dipoles, hydrogen bonding, multi-polar and dispersive forces [10]. Ultrasonic propagation parameters yield valuable information regarding the behaviour of liquid systems because intermolecular and intramolecular association, complex formation, dipolar interactions and related structural changes affect the compressibility of the system which in turn produces corresponding variations in ultrasonic velocity [11]. The different acoustical parameters interpret the nature and strength of molecular interaction that exist in the system [12]. The intermolecular interactions influence the structural arrangement along with the shape of the molecules [13, 14].

In the present study, an attempt has been made to investigate the behaviour of binary mixtures of chloroform and

methanol by measuring ultrasonic velocity, density and viscosity at 295K. From the measured data various derived acoustical parameters are computed and the results are interpreted in the light of molecular interaction.

MATERIALS AND METHODS

In the present study of molecular interactions of binary mixtures, chloroform of molecular weight 119.5 g/mol. were dissolved in methanol of molecular weight 32 g/mol. Mole fraction of chloroform (X_1) is decreased from 0.9 to 0.1 whereas mole fraction of methanol (X_2) is increased from 0.1 to 0.9.

The velocity of mixed solutions of chloroform and methanol at various concentrations was measured with the help of ultrasonic interferometer (Mittal enterprises) at the frequency of 2MHz. The density of the mixture was measured with the help of 25ml specific gravity bottle. An Oswald's viscometer whose capacity is 10ml was used for viscosity measurement of liquid mixtures. Distilled water had been used as a standard liquid.

(i) Velocity Measurement $U = \lambda \times f$
(ii)Density Measurement $\rho_2 = (W_2/W_1)\ \rho_1$
(iii) Viscosity Measurement $\eta_2 = \eta_1\ (t_2/t_1)\ (\rho_2/\rho_1)$

Other acoustical parameters derived from basic parameters can be defined as:

Acoustic impedance $Z = \rho \times U$
Adiabatic compressibility $\beta = 1/\ (U^2 \times \rho)$
Intermolecular free length $L_f = K_T \times \beta^{1/2}$ Where, K_T = Jacobson constant
Ultrasonic Attenuation $\alpha/f^2 = 8\pi^2\eta\ /3\rho U^3$
Relaxation Time $\tau = 4\beta\eta/3$
Effective Molecular Weight $M_{eff} = X_1M_1 + X_2\ M_2$
Free Volume $V_f = [M_{eff}\ U\ /\ K\eta]^{3/2}$ Where, K is temperature dependent constant.
Wada's Constant $W = (\beta)^{-1/7}M_{eff}/\ \rho$
Rao's Constant $R = U^{1/3}M_{eff}\ /\ \rho$
Molar Volume $V_m = M_{eff}/\ \rho$
Vander Waal's Constant $b = V_m[1-(RT/MU^2)\ \{(1 + (MU^2/3RT))^{1/2} - 1\}]$ Where, R is gas constant.
Internal Pressure (π_i) $\Pi_i = bRT\ [(k\eta/U)^{1/2}\ (\rho^{2/3}/\ M^{7/6})]$
Available Volume $V_a = M\ /\ \rho\ (1 - U/\ U_\infty)$ Where, U_∞ is velocity of sound at infinity.
Gibb's Free Energy $\Delta G = K_B\ T\ \ln\ (K_B\ T\ \tau/\ h)$
Enthalpy $H = V_m \times \pi_i$

RESULTS AND DISCUSSION

The experimental values of ultrasonic velocity, density and viscosity for the binary mixtures of Chloroform and methanol in different mole fractions at constant temperature 295 K are given in **Table 1**. From the standard parameters the values for derived parameters adiabatic compressibility, intermolecular free length and acoustic impedance, ultrasonic attenuation, relaxation time and effective molecular weight are shown in **Table 2** and**Table 3. Table 4** and **Table 5** gives the values of free volume, molar volume, available volume, Wada's Constant, Rao's Constant, Vander Waal's Constant. The values of internal pressure, Gibb's Free Energy and enthalpy listed in **Table 6.**

Table 1: Experimental values of ultrasonic velocity, density and viscosity of chloroform + methanol at different concentrations at temperature 295 K and frequency 2MHz

Mole fraction		Ultrasonic velocity (U) m/s	Density (ρ) Kg/m^3	Viscosity (η) × 10^{-3} Ns/m
X_1	X_2			
0.9	0.1	978.8	1289.744	1.102
0.8	0.2	981.2	1236.938	1.016
0.7	0.3	983.2	1191.176	1.051
0.6	0.4	992.4	1168.435	1.101
0.5	0.5	1008.4	1091.552	1.094
0.4	0.6	985.2	1045.054	1.000
0.3	0.7	1112.4	990.327	0.941
0.2	0.8	1116.8	945.889	0.923
0.1	0.9	1084	902.061	0.880

Table 2: Calculated values of adiabatic compressibility, intermolecular free length and acoustic impedance

Mole Fraction		Adiabatic compressibility (β) N/m^2 × 10^{-10}	Intermolecular Free Length (L_f) Å	Acoustic Impedance (Z) Kg m^{-2} s^{-1} × 10^5
X_1	X_2			
0.9	0.1	8.092	0.5964	12.624
0.8	0.2	8.397	0.6075	12.136
0.7	0.3	8.684	0.6178	11.711
0.6	0.4	8.690	0.6180	11.595
0.5	0.5	9.009	0.6292	11.007
0.4	0.6	9.858	0.6582	10.295
0.3	0.7	8.160	0.5988	11.016
0.2	0.8	8.476	0.6103	10.563
0.1	0.9	9.434	0.6439	9.778

Table 3: Values of ultrasonic attenuation, relaxation time and effective molecular weight

Mole Fraction		Ultrasonic Attenuation (α/f^2) s^2 m^{-1} × 10^{-14}	Relaxation Time (τ) s × 10^{-12}	Effective Molecular Weight (M_{eff}) gm
X_1	X_2			
0.9	0.1	2.396	1.1890	110.75
0.8	0.2	2.286	1.1378	102.00
0.7	0.3	2.438	1.2158	93.25
0.6	0.4	2.535	1.2762	84.50
0.5	0.5	2.571	1.3146	75.75
0.4	0.6	2.631	1.3148	67.00
0.3	0.7	1.815	1.0242	58.25
0.2	0.8	1.842	1.0433	49.50
0.1	0.9	2.015	1.1078	40.75

Table 4: Calculated values of free volume, molar volume and available volume

Mole Fraction		Free Volume (V_f) m^3/ mol × 10^{-3}	Molar Volume (V_m) m^3/ mol × 10^{-2}	Available Volume (V_a) m^3/ mol × 10^{-2}
X_1	X_2			
0.9	0.1	3.482	8.586	3.333
0.8	0.2	3.490	8.246	3.189
0.7	0.3	2.913	7.828	3.017
0.6	0.4	2.372	7.232	2.746
0.5	0.5	2.082	6.939	2.565
0.4	0.6	1.914	6.411	2.463
0.3	0.7	2.039	5.881	1.792
0.2	0.8	1.655	5.233	1.580
0.1	0.9	1.268	4.517	1.456

Table 5: Values of Wada's Constant, Rao's Constant, Vander Waal's Constant

Mole Fraction		Wada's Constant (W)	Rao's Constant (R)	Vander Waal's Constant
X_1	X_2	$(m^3/mol)(Pa)^{1/7}$	$(m^3/mol)(m/s)^{1/3}$	(b) m^3/mol
0.9	0.1	1.708	0.852	0.085
0.8	0.2	1.632	0.819	0.082
0.7	0.3	1.542	0.778	0.078
0.6	0.4	1.424	0.721	0.072
0.5	0.5	1.359	0.696	0.069
0.4	0.6	1.240	0.693	0.063
0.3	0.7	1.169	0.609	0.058
0.2	0.8	1.034	0.543	0.052
0.1	0.9	0.879	0.464	0.045

Table 6: Calculated values of internal pressure, Gibb's Free Energy and enthalpy

Mole Fraction		Internal Pressure (π_i)	Gibb's Free Energy	Enthalpy (H)
X_1	X_2	$Pa \times 10^5$	$(\Delta G)\ KJ\ mol^{-1} \times 10^{-21}$	$J/mol \times 10^4$
0.9	0.1	1.663	8.098	1.428
0.8	0.2	1.707	7.916	1.407
0.7	0.3	1.876	8.186	1.614
0.6	0.4	2.119	8.384	1.532
0.5	0.5	2.275	8.504	1.578
0.4	0.6	2.466	8.505	1.581
0.3	0.7	2.557	7.488	1.504
0.2	0.8	2.964	7.563	1.551
0.1	0.9	3.573	7.808	1.614

Plot of ultrasonic velocity versus mole fraction is shown in **Figure 1.**It decreases with increase in concentration of chloroform and this variation in ultrasonic velocity is due to the variation in intermolecular free length.

From **Figure 2 & 3** it can be seen that density and viscosity of the liquid mixture increases. Increase in density shows the presence of large number of molecules in the mixture. Increase in viscosity indicates presence of strong intermolecular forces. An increase in viscosity values with increasing concentration of chloroform suggests more association between solute and solvent molecules.

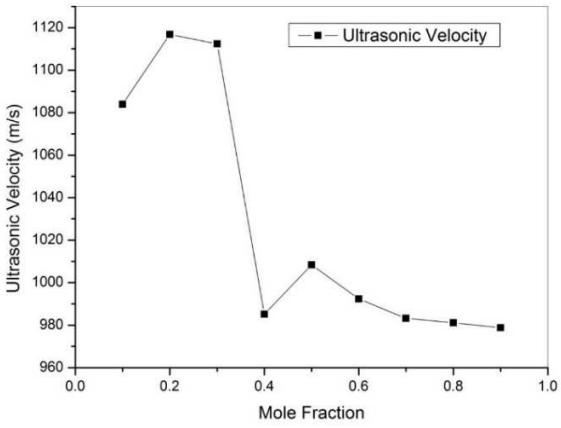

Figure 1: Ultrasonic velocity versus mole fraction at temperature 295K

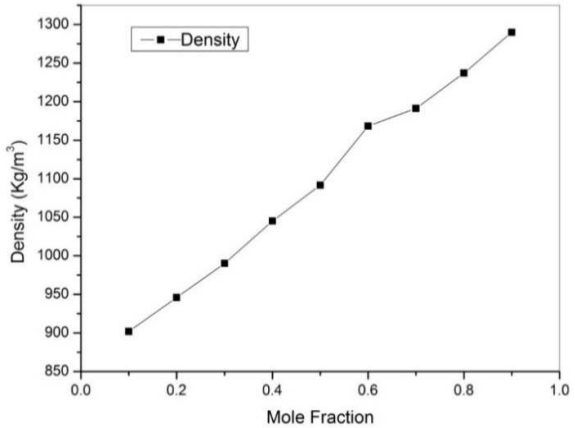

Figure 2: Density versus mole fraction at temperature 295K

The adiabatic compressibility decreases with increasing concentration which is due to the strong molecular interaction among the solute and solvent molecules shown in **Figure 4**. **Figure 5**depicts the variation in intermolecular free length. This decrease in free length is due to the decreased adiabatic compressibility which brings the molecules to a closer packing. The linear variation in acoustic impedance indicates the absence of specific interaction like complex formation in thebinary mixture as shown in **Figure 6.**It can be seen from the mathematical relations for acoustic

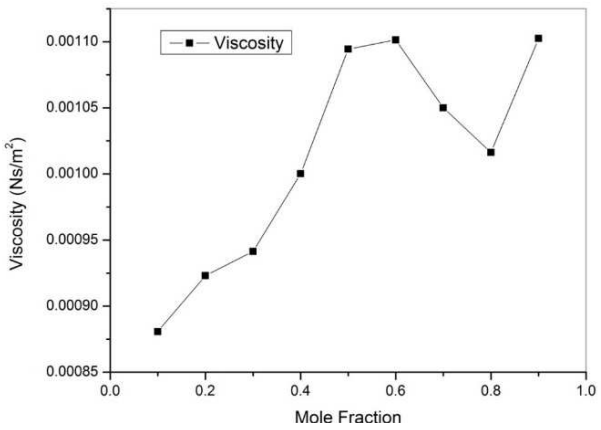

Figure 3: Viscosity versus mole fraction at temperature 295K

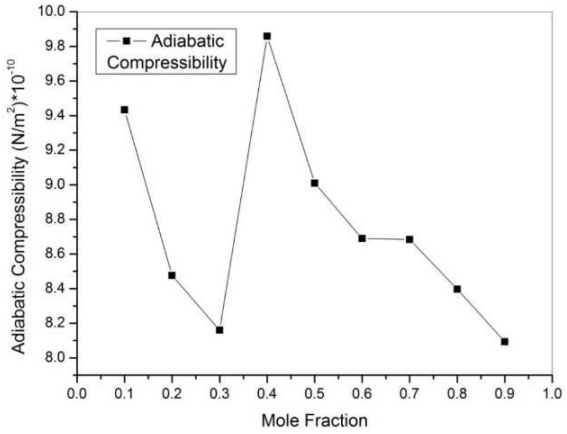

Figure 4: Adiabatic compressibility versus molefraction of at 295K

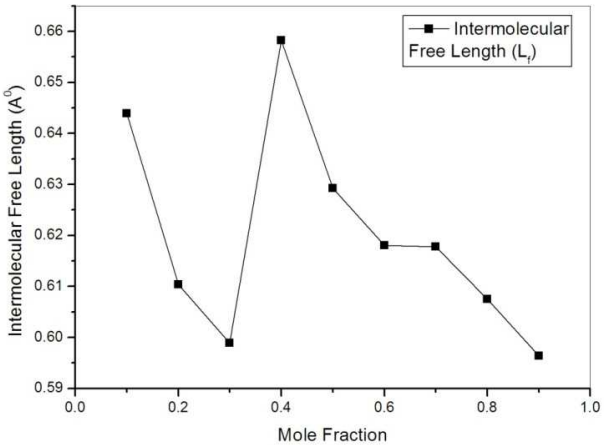

Figure 5: Intermolecular free length versus mole fraction at 295K

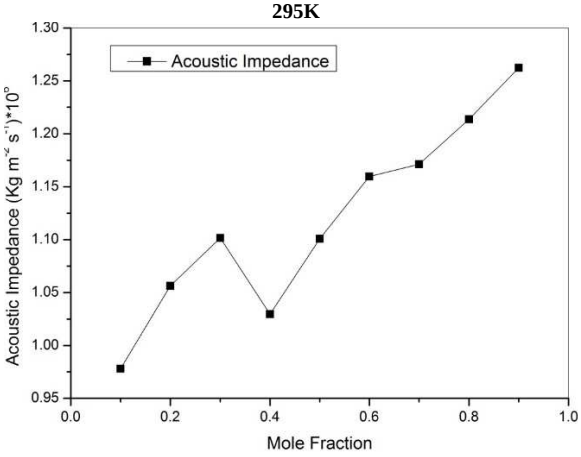

Figure 6: Acoustic impedance versus mole fraction at 295K

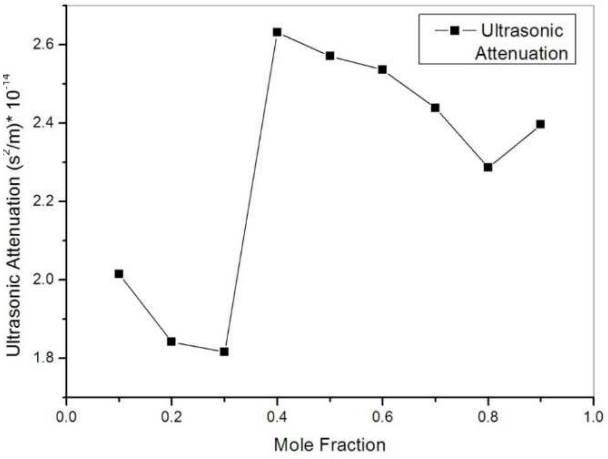

Figure 7: Ultrasonic attenuation versus mole fraction at 295K

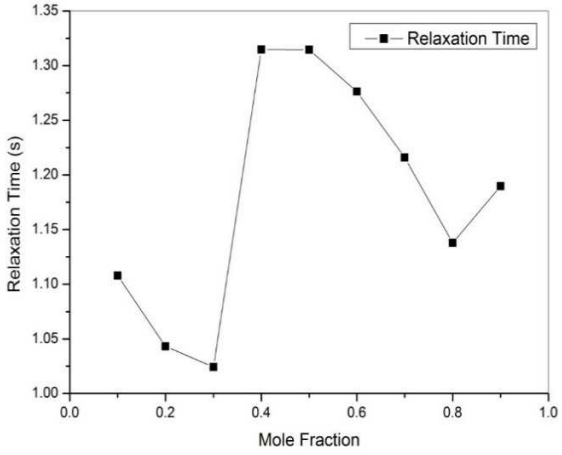

Figure 8: Relaxation time versus mole fraction at 295K

impedance (Z=ρU) andadiabatic compressibility ($\beta = 1/ \rho U^2$) that they must show opposite behavior and adiabatic compressibility (β) and intermolecular free length ($L_f = K_T \times \beta^{1/2}$) should exhibit same behavior which is in agreement with the experimental results.

Figure 7 and **Figure 8** illustrate the linear behaviour of ultrasonic attenuation and relaxation time with mole fraction and the trend of these parameters is almost same with best results obtained between 0.4 to 0.8 ranges of mole

fraction. As seen from the experimental results velocity decreases which results in the decrease of ultrasonic attenuation. The decrease in relaxation time indicates that the viscous force has no effect on it.

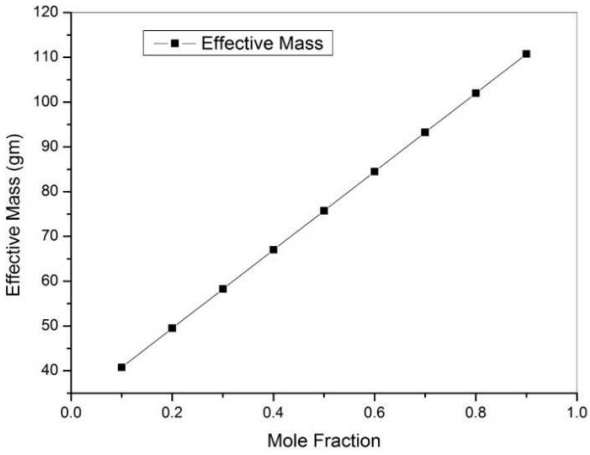

Figure 9: Effective molecular mass versus mole fraction for chloroform + methanol at 295K

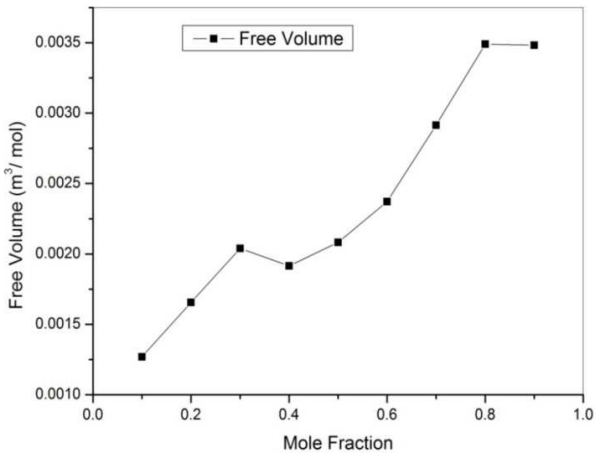

Figure 10: Free Volume versus mole fraction for chloroform + methanol at 295K

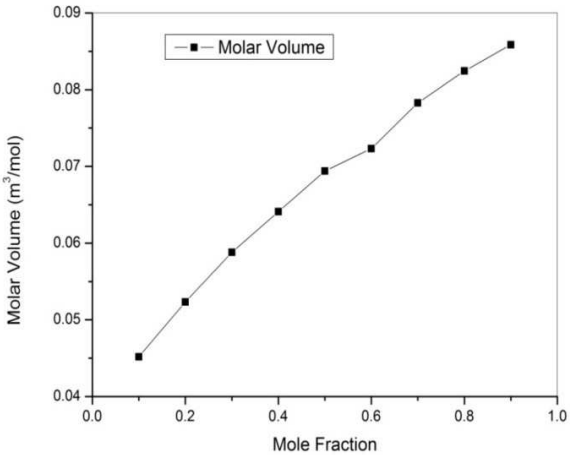

Figure 11: Molar Volume versus mole fraction at 295K

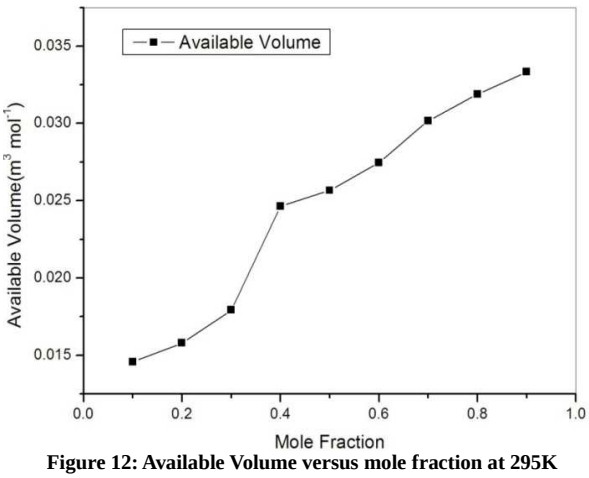

Figure 12: Available Volume versus mole fraction at 295K

The plot between effective molecular mass and mole fraction shown in **Figure 9** illustrates that effective mass increases with increase in mole fraction which indicates the presence of heavier molecules in the binary mixture.The free volume increases with increase in concentration (shown in **Figure 10**) suggests that there is a weak interaction among the solute and solvent molecules.

The molar volume also increases with increase in concentration as shown in **Figure 11**. Available volume is a measure of compactness and strength of bonding between the molecules of the binary liquid mixture. **Figure 12** predicts that available volume increases with increase in concentration of chloroform which shows that there is weak bonding between the molecules of the liquid mixture.

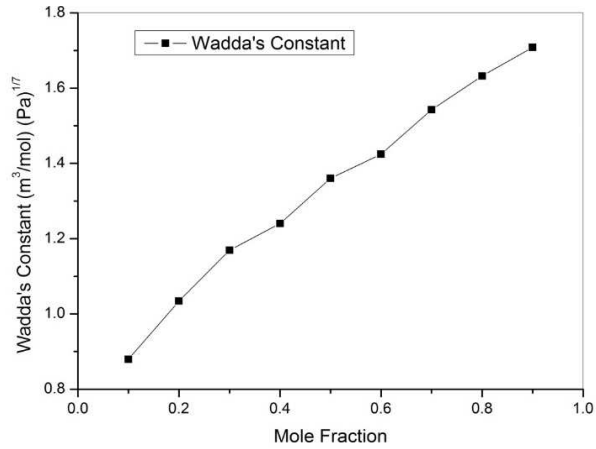

Figure 13: Wada's Constant versus mole fraction at 295K

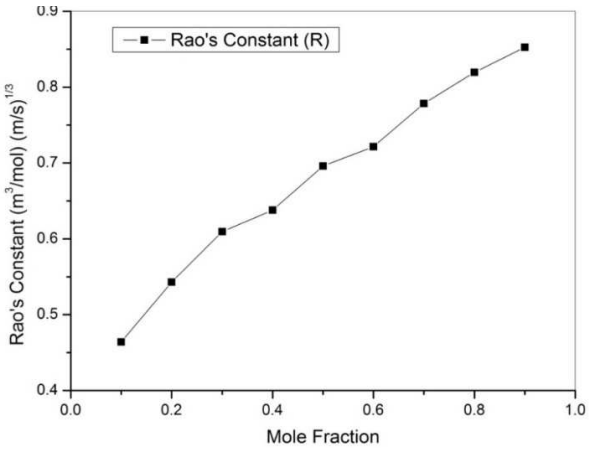

Figure 14: Rao's Constant versus mole fraction at 295K

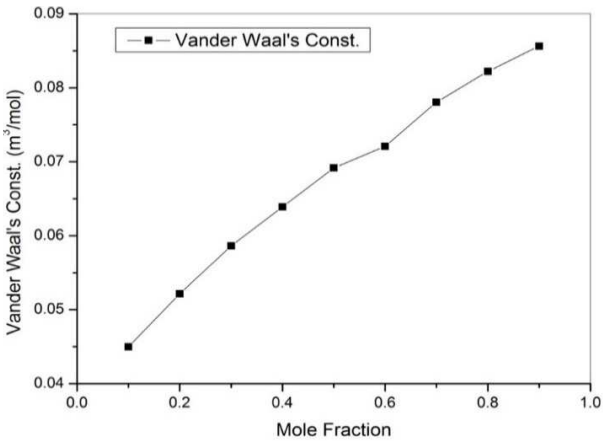

Figure 15: Vander Waal's constant versus mole fraction at 295K

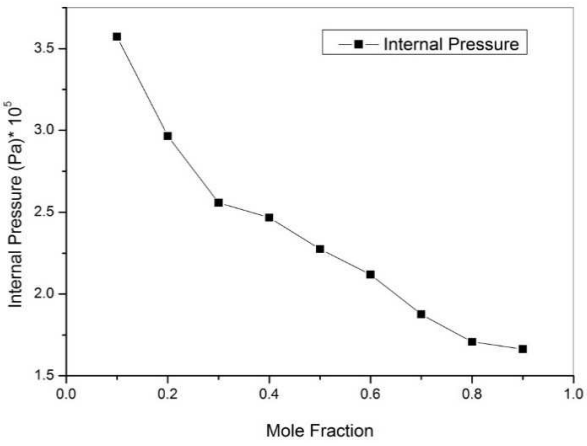

Figure 16: Internal pressure versus mole fraction at 295K

All the three constants: Wada's Constant, Rao's Constant and Vander Waal's Constant are increasing with increase in mole fraction and is displayed in **Figures 13, 14 & 15** respectively.It was reported that if the variation in Rao's Constant and Wada's Constant is linear, then it shows that there is an absence of complex formation in the mixture and so is found in the present investigation which means that there is no complex formation in the mixture of Chloroform and Methanol. Increase in Vander Waal's Constant reveals that the molecules are not very close and hence the interaction is decreasing.

The internal pressure gives information regarding the nature and strength of force existing between the molecules. Due to decrease in internal pressure of the liquid mixture as shown in **Figure 16**, there is an increase in the values of free volume which shows that the strength of interaction among the molecules decreases gradually with increase in concentration and hence weak interaction between the molecules is found.

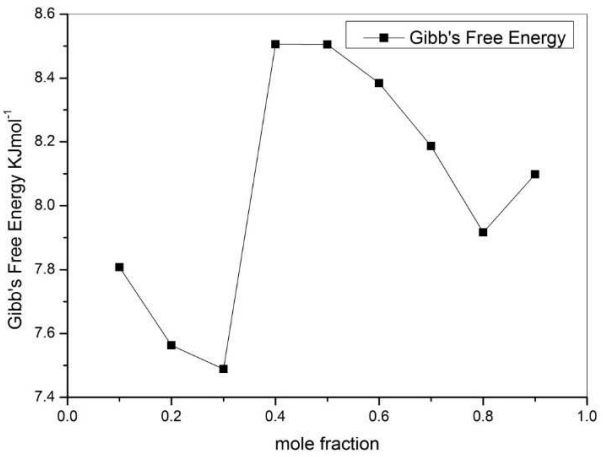

Figure 17: Gibb's Free Energy versus mole fraction at 295K

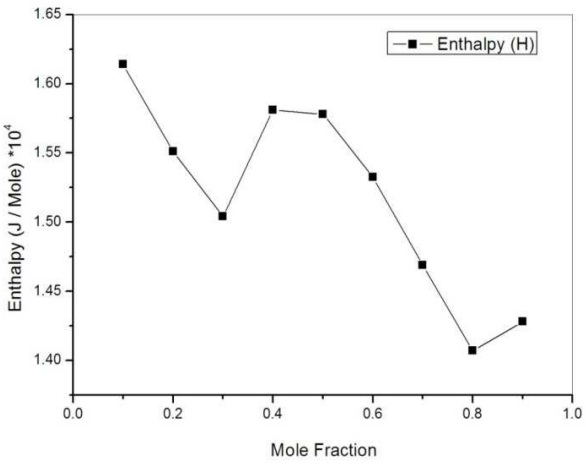

Figure 18: Enthalpy versus mole fraction at temperature 295K

The Gibb's free energy decreases with increase in concentration of solute molecules (**Figure 17**) which confirms the hydrogen bonding formation in binary liquid mixtures. [3]**Figure 18** gives the plot between enthalpy and mole fraction and decrease in the values of enthalpy indicates the weak interaction among the solute and solvent molecules.

CONCLUSION

The ultrasonic study of binary mixtures of chloroform and methanol shows the presence of molecular interactions between the molecules of the mixture. The ultrasonic velocity decreases with increase in concentration which is due to the increase in intermolecular free length of the mixture. The density and viscosity increases with increase in mole fraction. Adiabatic compressibility, intermolecular free length, ultrasonic attenuation and relaxation time decreases with increase in concentration. This decrease in acoustical parameters indicates that there is a weak interaction between the molecules of the mixture. Wada's constant, Rao's constant and Vander Waal's constant show linear variation with increase in mole fraction which indicates the absence of complex formation in the mixture.

REFERENCES

[1] S.C. Bhatt, R.S.Rawat and B.S. Semval ;"*Journal of Acoustical Society of India*", 27, 297-300. **(1999)**
[2] M. K. Gangwarand A. K. Saxena; "*Research Journal of Chemical Sciences*" 3(2), 27-30. **(2013)**
[3] A. A. Mistry, V. D. Bhnadarkar and O. P. Chimankar; "*Advances in Applied Science Research*", 4(2), 54-59. **(2013)**
[4] K. Saravanakumar, R. Baskaran, and T. R. Kubendran Russian "*Journal of Physical Chemistry* "A, 86(13), 1947–1952.**(2012)**
[5] G. R. Bedare, V. D. Bhandakkar and B. M. Suryavanshi;"*European Journal of Applied Engineering and Scientific Research"* 1 (1), 1-4.**(2012)**
[6] R. R. Amrutia, N. M. Mehta, F. D. Karia and P. H. Parsania; "*Journal of Scientific and Industrial Research*" 65, 905-911. **(2006)**
[7] M. K. Praharaj, A.Satapathy, P. Mishra and S. Mishra; "*Journal of Chemical and Pharmaceutical Research*" 5(1), 49-56. **(2013)**
[8] V. D. Bhandakkar, V. R. Bhat, O. P. Chimankarand A. W. Asole; "*Advances in Applied Science Research*" 5(2), 80-85. **(2014)**
[9] M. K. Rawat and Sangeeta; "*Indian Journal of Pure and Applied Physics*" 46(3), 187-192. **(2008)**
[10] E. Jasmine, V. Rani, K. Kannagi, R.Padmavathy and N. Radha; "*Journal of Basic and Applied Physics*" 1, 96-101.**(2012)**
[11] P. K. Singh and S.C. Bhatt;"*Applied Physics Research*" 2(1), 35-41. **(2010)**
[12] P.Tabhane, O. P. Chimankar, C. M. Dudhe and Vilas A. Tabhane; "*Der Chemica Sinica*", 3(4), 944-947. **(2012)**
[13] M.P. Wadekar; "*Journal of Chemical and Pharmaceutical Research*" 5(8), 37-41. **(2013)**
[14] Kaur B. and Juglan K. C; *Journal of Polymer Engineering*, Vol. 33, pp.851-856 (**2013**).