

# Acoustical studies of some synthesized Schiff base derivatives in dimethylsulphoxide at 303.15 K, by ultrasonic velocity measurement

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## ABSTRACT

The density, viscosity and sound velocity of five Schiff bases (1-5) derivatives in DMSO solutions have been studied at 303.15 K over a wide range of concentration. From these experimental data, some acoustical parameters such as Molar volume ( $V_m$ ), Specific Acoustic Impedance ( $Z$ ), Adiabatic compressibility ( $\beta_{ad}$ ), Intermolecular Free Length ( $L_f$ ), Rao's Constant ( $R$ ), Molar compressibility ( $W$ ), Relaxation time ( $\tau$ ), van der Waals constant ( $b$ ), Relaxation strength ( $r$ ), Relative association ( $R_A$ ), Isothermal compressibility ( $\beta_T$ ), Isothermal expansion co-efficient ( $\alpha$ ), Free volume ( $V_f$ ) and Internal pressure ( $\pi_i$ ) and Ultrasonic attenuation ( $\alpha/f^2$ ) have been evaluated. A fairly good correlation between a given parameter and concentration is observed. The results are interpreted in terms of molecular interactions like solvent-solvent, solvent-solute and solute-solute interactions.

**Keywords:** Density; Viscosity; Ultrasonic velocity; DMSO; Acoustical parameters; Molecular interactions

## 1. INTRODUCTION

In the recent years, measurements of the Ultrasonic velocity are helpful to interpreted solute-solvent, ion-solvent interaction in aqueous and non aqueous medium [1]. Ultrasonic investigations find extensive applications in characterizing aspects of thermodynamics and physico chemical behavior of solutions of organic compounds. The measurement of ultrasonic speed enables to accurate determination of some useful parameters, which are highly sensitive to molecular interactions [2].

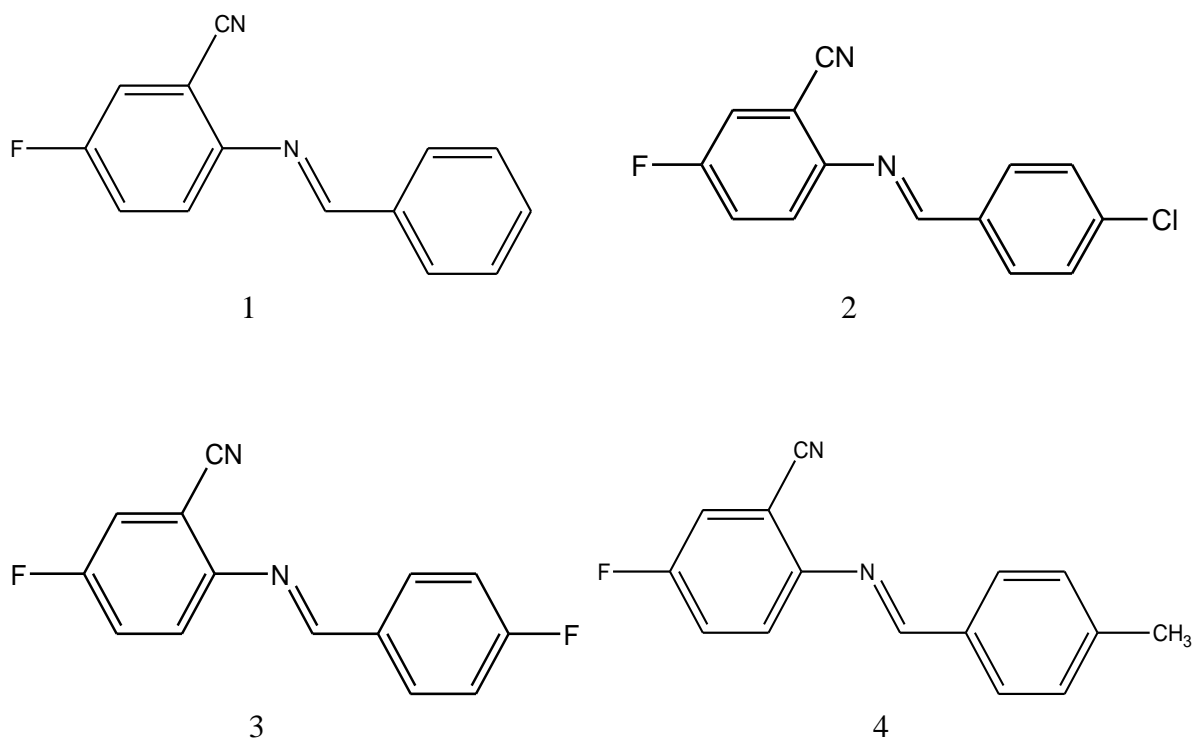
Literature survey on ultrasound velocity measurement shows that very little work has been done for solid organic compounds. The ultrasonic velocity along with other experimental data such as density and viscosity, furnish wealth of information about the interaction between ions, dipoles, hydrogen bonding, multi-polar and dispersive forces. This molecular interactions between like and unlike molecules are influenced by structural arrangement along with shape and size of the molecules [3].

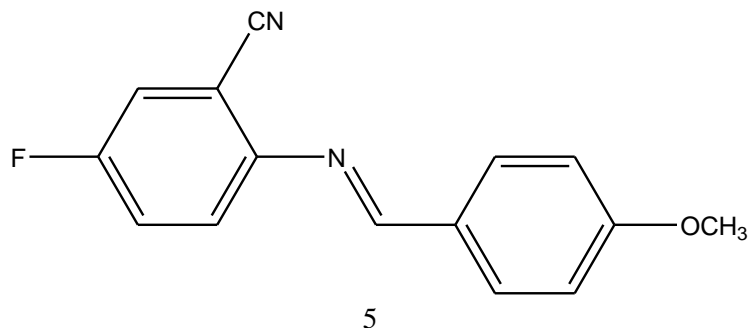
We have synthesized some new Schiff base derivatives. In continuation of our work we intended to investigate the solute-solute, solute-solvent molecular interactions of these newly synthesized Schiff base derivatives in DMSO. By simply measuring density of liquid and its corresponding ultrasonic velocity, many parameters like Molar volume ( $V_m$ ), Specific Acoustic Impedance ( $Z$ ), Adiabatic compressibility ( $\beta_{ad}$ ), Intermolecular Free Length ( $L_f$ ), Rao's Constant ( $R$ ), Molar compressibility ( $W$ ), Relaxation time( $\tau$ ), vander Waals constant ( $b$ ), Relaxation strength ( $r$ ), Relative association ( $R_A$ ) Isothermal compressibility ( $\beta_T$ ), Isothermal expansion co-efficient ( $\alpha$ ), Free volume ( $V_f$ ) and Internal pressure ( $\pi_i$ ) and Ultrasonic attenuation ( $\alpha/f^2$ ) etc. can be determined. From the observations of these properties the molecular interactions are predicted.

## 2. EXPERIMENTAL

The solvent used in the present work of AR grade and were purified according to the standard procedure described in the literature [4]. The Compounds were recrystallized before use. The structure of the synthesizsed compounds are given in Scheme 1.

Solutions of different molarity were prepared for each binary system. The ultrasonic velocity in the mixture was measured using a variable path fixed frequency ultrasonic interferometer working at 2 MHz frequency (Mittal enterprises, New Delhi). The accuracy of sound velocity was  $\pm 0.1 \text{ ms}^{-1}$ . The density was determined at the experimental temperature using 10 ml capacity specific gravity bottle immersed in a thermostatic bath (accuracy  $+0.01 \text{ }^\circ\text{C}$ ).





**Scheme 1.** Structures of synthesized Schiff base Derivatives [1-5].

The volume of the bottle at the experimental temperatures, viz. 303.15 K was ascertained using doubly distilled water. The densities of water at these temperatures were obtained from literature. The viscosity of pure liquids and liquid mixtures at 303.15 K were determined using an Ostwald viscometer.

### 3. RESULTS AND DISCUSSION

Ultrasonic velocity ( $u$ ), density ( $\rho$ ) and viscosity ( $\eta$ ) of the solutions were obtained using the relations;

$$\text{Ultrasonic velocity } u = n \times \lambda \text{ ----- (1)}$$

$$\text{Density } \rho = m / V \text{ ----- (2)}$$

$$\text{Viscosity } \eta = [t_2 / t_1] \times [\rho_2 / \rho_1] \times \eta_1 \text{ -----(3)}$$

where,  $n$  &  $\lambda$  are frequency and wavelength;  $V$  is the volume of the solution;  $\eta_1$  &  $\eta_2$  are the viscosities of the water and solutions;  $t_1$ ,  $t_2$  are time of flow water and solution and  $\rho_1$  &  $\rho_2$  are the densities of the water and solution

From the experimental data of ultrasonic velocity ( $u$ ), density ( $\rho$ ) and viscosity ( $\eta$ ), the various thermodynamic parameters such as adiabatic compressibility ( $\beta_{ad}$ ), intermolecular free length ( $L_f$ ), specific acoustical impedance ( $Z$ ), Rao's molar sound function ( $R$ ), Vander Waals constant ( $b$ ), etc., were evaluated using the following standard equations [5-17].

1. Adiabatic compressibility,  $\beta_{ad} = 1/u^2 \rho$
2. Intermolecular free length,  $L_f = K/u\rho^{1/2}$
3. Relative association  $(R.A) = \left(\frac{\rho}{\rho_0}\right) \left(\frac{C_0}{C}\right)^{1/3}$
4. Specific Acoustic impedance,  $Z = P_e/C$

5. Viscous relaxation time,  $\tau = \frac{4}{3}\beta\eta$
6. Relaxation strength,  $r = 1 - \left(\frac{u}{u_\alpha}\right)^2$
7. Rao's constant or molar sound velocity,  $R = Vu^{1/3}$
8. Wada's constant,  $W = \frac{M}{\rho}K_s^{1/7}$
9. Ultrasonic attenuation,  $\frac{\alpha}{f^2} = \frac{8\pi^2\eta}{3u^3\rho}$
10. Vander Waal's constant,  $b = \frac{M}{\rho} \left\{ 1 - \left(\frac{RT}{MC^2}\right) \left[ 1 + \left(\frac{MC^2}{RT}\right)^{1/2} - 1 \right] \right\}$
11. Isothermal compressibility,  $\beta_T = \frac{1.71 \times 10^{-3}}{T^{4/9}u^{1/2}\rho^{1/3}}$
12. Isothermal expansion co-efficient,  $\alpha = (0.0191\beta_T)^{1/4}$
13. Internal pressure,  $\pi_i = \frac{\alpha T}{\beta_T}$
14. Free volume,  $V_f = \left(\frac{bRT}{\pi_i}\right)^3 \left(\frac{1}{V^2}\right)$

Some of these calculated parameters are given in Table 1-4 for the studied compounds in DMSO. Graphical representations of Density, Speed of sound, Viscosity, Molar volume (Vm), Specific Acoustic Impedance (Z), Adiabatic compressibility ( $\beta_{ad}$ ), Intermolecular Free Length ( $L_f$ ), Rao's Constant (R), Molar compressibility (W), Relaxation time( $\tau$ ), vander Waals constant (b), Relaxation strength (r), Relative association ( $R_A$ ) and Ultrasonic attenuation ( $\alpha/f^2$ ) are given in Fig 1-5. Figure 1 show the variation of ultrasound velocity ( $U$ ) with concentration in DMSO solutions. It is observed that overall ultrasonic velocity ( $U$ ) increases with concentration for all the compounds in DMSO solvent. The velocity depends on intermolecular free length ( $L_f$ ). The velocity increases with decrease in  $L_f$  or vice versa. It is evident from Table 2 that  $L_f$  decreases continuously, which suggests that there is strong interaction between solvent and compound molecules.

Specific acoustic impedance is defined as the impedance offered to the sound wave by the components of the mixture. Acoustic impedance increases with increase in concentration. Increasing trend of acoustic impedance further support the possibility of molecular interaction due to hydrogen bonding between Schiff base and DMSO. Specific acoustic impedance is directly proportional to ultrasonic velocity and inversely proportional to adiabatic compressibility and shows similar behaviour to that of ultrasonic velocity and opposite to that of adiabatic compressibility.

**Table 1.** Ultrasonic velocity (U), Density( $\rho$ ), Viscosity ( $\eta$ ) and Molar volume ( $V_m$ ) of Schiff base derivatives with DMSO at 303.15 K.

Concentration (M)	Schiff base derivatives (1-5)			
	U (m/s)	$\rho$ (Kg/m <sup>3</sup> )	$\eta$ (mPa.s)	$V_m$ (10 <sup>-6</sup> m <sup>3</sup> /mole)
<b>Compound 1</b>				
0.02	1503	963.1	0.9631	84.16
0.04	1506	979.6	0.9796	85.72
0.06	1508	998.6	0.9986	87.02
0.08	1521	1013.9	1.0139	88.59
0.1	1524	1034.2	1.0342	89.67
<b>Compound 2</b>				
0.02	1494	962.7	0.9627	84.91
0.04	1503	979.3	0.9793	87.16
0.06	1505	998.4	0.9984	89.11
0.08	1507	1014.3	1.0143	91.27
0.1	1509	1024.8	1.0248	93.86
<b>Compound 3</b>				
0.02	1500	964.2	0.9642	84.43
0.04	1504	984.3	0.9843	86.04
0.06	1509	993.9	0.9939	88.52
0.08	1510	1001.2	1.0012	91.15
0.1	1513	1021.5	1.0215	92.55
<b>Compound 4</b>				
0.02	1484	979.1	0.9791	83.07
0.04	1488	996.8	0.9968	84.81
0.06	1490	998.4	0.9984	87.88
0.08	1500	1013.4	1.0134	89.74
0.1	1507	1033.4	1.0334	91.1
<b>Compound 5</b>				
0.02	1499	977.3	0.9773	83.55
0.04	1508	997.0	0.9970	85.43
0.06	1514	1016.0	1.0160	87.3
0.08	1515	1034.6	1.0346	89.14
0.1	1519	1052.5	1.0525	90.97

**Table 2.** Specific Acoustic Impedance (Z), Adiabatic compressibility ( $\beta_{ad}$ ), Intermolecular Free Length ( $L_f$ ), Rao's Constant (R) and Molar compressibility (W) of Schiff base derivatives with DMSO at 303.15 K.

Concentration (M)	Schiff base derivatives (1-5)				
	Z ( $10^3 \text{Kg/m}^2\text{s}$ )	$\beta_{ad}$ ( $10^{-10} \text{Pa}^{-1}$ )	$L_f$ ( $10^{-10} \text{m}$ )	R ( $\text{m}^3/\text{mole})(\text{m/s})^{1/3}$	W ( $\text{m}^3/\text{mole})(\text{N/m}^2)^{1/7}$
<b>Compound 1</b>					
0.02	1447.539	4.5963	0.4494	0.964	1.8157
0.04	1475.278	4.5009	0.4447	0.9826	1.855
0.06	1505.889	4.4035	0.4399	0.9979	1.8889
0.08	1542.142	4.2633	0.4328	1.0188	1.9319
0.1	1576.121	4.1631	0.4277	1.0319	1.9622
<b>Compound 2</b>					
0.02	1438.274	4.6538	0.4522	0.9707	1.8286
0.04	1471.888	4.5202	0.4457	0.9984	1.8848
0.06	1502.592	4.4220	0.4408	1.0211	1.9331
0.08	1528.55	4.3411	0.4368	1.0464	1.9852
0.1	1546.423	4.2853	0.4339	1.0765	2.0453
<b>Compound 3</b>					
0.02	1446.3	4.6094	0.4501	0.9665	1.8209
0.04	1480.387	4.4913	0.4443	0.9858	1.8625
0.06	1499.795	4.4185	0.4406	1.0153	1.9205
0.08	1511.812	4.3805	0.4387	1.0457	1.98
0.1	1545.53	4.2764	0.4335	1.0625	2.0174
<b>Compound 4</b>					
0.02	1452.984	4.6377	0.4514	0.9475	1.7899
0.04	1483.238	4.5309	0.4462	0.9682	1.8334
0.06	1487.616	4.5115	0.4453	1.0037	1.901
0.08	1520.1	4.3856	0.4390	1.0272	1.9491
0.1	1557.334	4.2609	0.4327	1.0445	1.9868
<b>Compound 5</b>					
0.02	1464.973	4.5537	0.4473	0.9562	1.8049
0.04	1503.476	4.4106	0.4402	0.9797	1.854
0.06	1538.224	4.2939	0.4344	1.0024	1.9019
0.08	1567.419	4.2111	0.4302	1.0237	1.9473
0.1	1598.748	4.1177	0.4254	1.0457	1.9936

**Table 3.** Relaxation time( $\tau$ ), van der Waals constant (b), Relaxation strength (r), Relative association ( $R_A$ ) and Ultrasonic attenuation ( $\alpha/f^2$ ) of Schiff base derivatives with DMSO at 303.15 K.

Concentration (M)	Schiff base derivatives (1-5)				
	$\tau$ ( $10^{-10}$ sec)	b ( $m^3/mole$ )	r	$R_A$	$\alpha/f^2$ ( $10^{-12}$ sec)
<b>Compound 1</b>					
0.02	5.9022	0.0839	0.1175	0.8721	7.7437
0.04	5.8788	0.0855	0.1140	0.8864	7.6975
0.06	5.8632	0.0868	0.1116	0.9032	7.6669
0.08	5.7634	0.0884	0.0963	0.9144	7.4720
0.1	5.7407	0.0895	0.0927	0.9321	7.4280
<b>Compound 2</b>					
0.02	5.9736	0.0847	0.1281	0.8734	7.8845
0.04	5.9022	0.0869	0.1175	0.8867	7.7437
0.06	5.8866	0.0889	0.1152	0.9036	7.7129
0.08	5.871	0.0910	0.1128	0.9176	7.6822
0.1	5.8554	0.0936	0.1105	0.9267	7.6517
<b>Compound 3</b>					
0.02	5.9259	0.0842	0.1210	0.8736	7.7903
0.04	5.8944	0.0858	0.1164	0.8911	7.7283
0.06	5.8554	0.0883	0.1105	0.8988	7.6517
0.08	5.8477	0.0909	0.1093	0.9052	7.6365
0.1	5.8245	0.0923	0.1057	0.9229	7.5912
<b>Compound 4</b>					
0.02	6.0544	0.0828	0.1397	0.8903	8.0450
0.04	6.0218	0.0846	0.1351	0.9056	7.9803
0.06	6.0057	0.0877	0.1327	0.9066	7.9482
0.08	5.9259	0.0895	0.1210	0.9182	7.7903
0.1	5.871	0.0909	0.1128	0.9349	7.6822
<b>Compound 5</b>					
0.02	5.9338	0.0833	0.1222	0.8857	7.8059
0.04	5.8632	0.0852	0.1116	0.9018	7.6669
0.06	5.8168	0.0871	0.1046	0.9177	7.5761
0.08	5.8091	0.0889	0.1034	0.9343	7.5611
0.1	5.7786	0.0907	0.0986	0.9497	7.5016

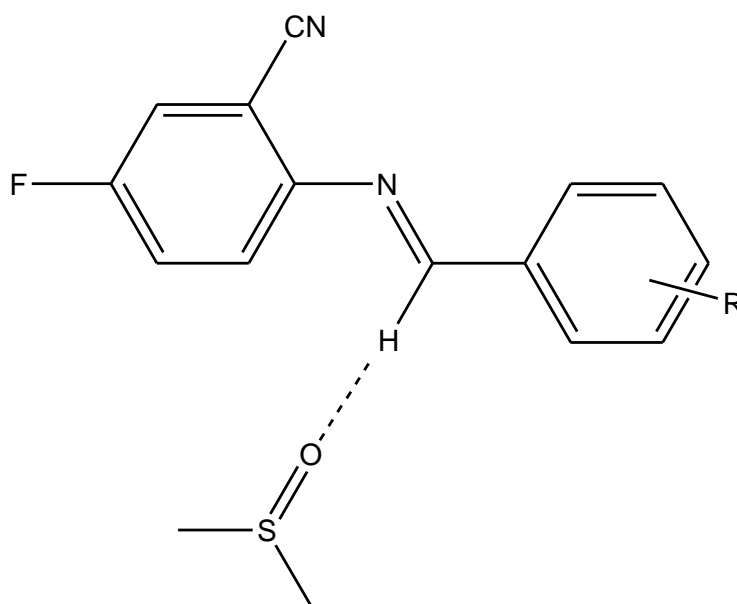
**Table 4.** Isothermal compressibility ( $\beta_T$ ), Isothermal expansion co-efficient ( $\alpha$ ), Free volume ( $V_f$ ) and Internal pressure ( $\pi_i$ ) of Schiff base derivatives with DMSO at 303.15 K

Concentration (M)	Schiff base derivatives (1-5)			
	$\beta_T$ ( $10^{-14}\text{Pa}^{-1}$ )	$\alpha$ ( $10^4\text{K}^{-1}$ )	$V_f$ ( $10^{-6}\text{m}^3/\text{mole}$ )	$\pi_i$ ( $10^6\text{Pa}$ )
<b>Compound 1</b>				
0.02	0.6279	1.0465	0.1606	4.8283
0.04	0.6113	1.0395	0.1656	4.7209
0.06	0.5943	1.0322	0.1697	4.6359
0.08	0.5725	1.0226	0.1766	4.5209
0.1	0.5553	1.0149	0.1804	4.4526
<b>Compound 2</b>				
0.02	0.6358	1.0498	0.1613	4.7929
0.04	0.6140	1.0407	0.1693	4.6351
0.06	0.5968	1.0333	0.1753	4.5140
0.08	0.5828	1.0272	0.1821	4.3865
0.1	0.5734	1.023	0.1903	4.2428
<b>Compound 3</b>				
0.02	0.6294	1.0471	0.1609	4.8146
0.04	0.6091	1.0386	0.1662	4.7034
0.06	0.5973	1.0335	0.1743	4.5431
0.08	0.5907	1.0306	0.1823	4.3889
0.1	0.5728	1.0227	0.1871	4.3072
<b>Compound 4</b>				
0.02	0.6300	1.0474	0.1545	4.9335
0.04	0.6119	1.0398	0.1601	4.8093
0.06	0.6089	1.0385	0.1692	4.6106
0.08	0.5890	1.0299	0.1763	4.4843
0.1	0.5685	1.0208	0.1816	4.3959
<b>Compound 5</b>				
0.02	0.6190	1.0428	0.1582	4.8758
0.04	0.5956	1.0328	0.1651	4.7365
0.06	0.5762	1.0243	0.1716	4.6092
0.08	0.5617	1.0177	0.1772	4.4972
0.1	0.5461	1.0106	0.1834	4.3860



This is further supported by adiabatic compressibility and relaxation strength ( $r$ ) values. The variation of adiabatic compressibility with concentration of these compounds is also shown (Fig. 2). Both adiabatic compressibility and relaxation strength. Table 2 and 3 are observed to decrease with concentration for all the compounds.

The decrease in adiabatic compressibility is attributed to the fact that the Schiff base molecules in dilute solutions are considerably ionized and these ions are firmly bound to surrounding solvent molecules. The orientation of solvent molecules around the ions is attributed to the influence of the electrostatic field of the ions, which lowers the compressibility of the Schiff base solution.

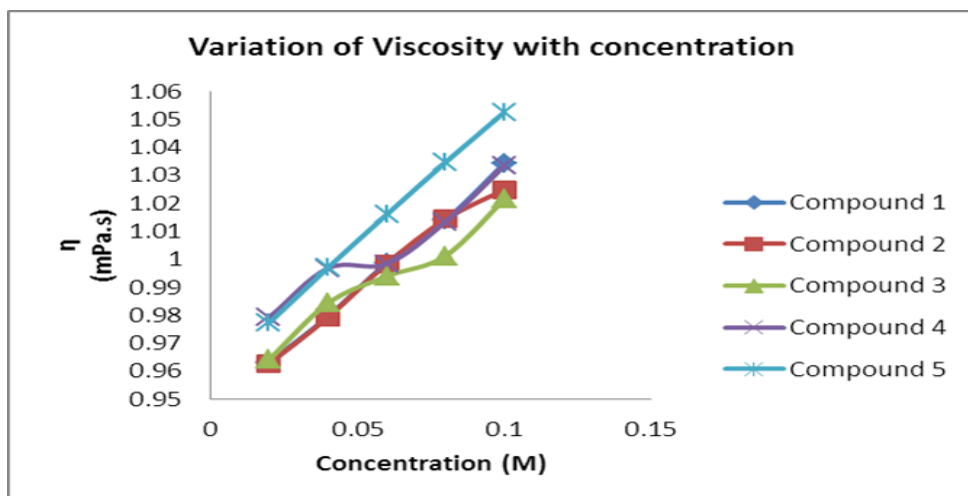
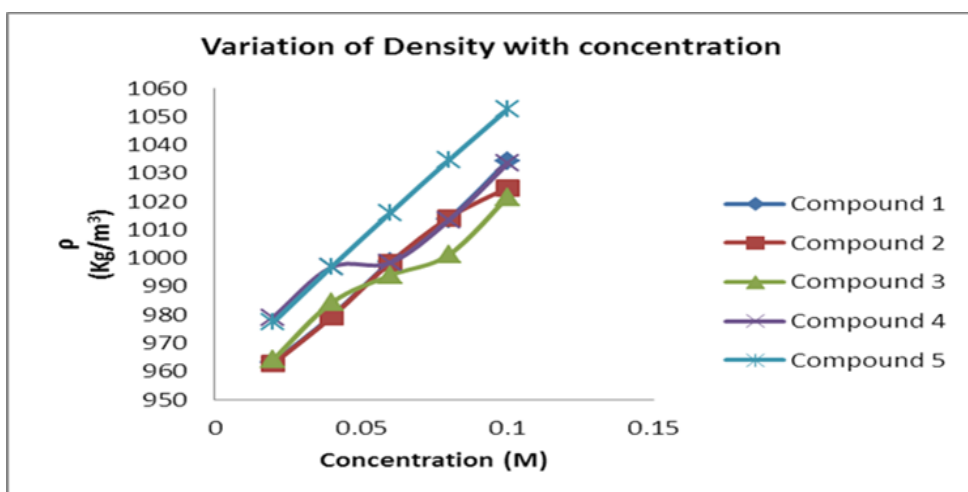
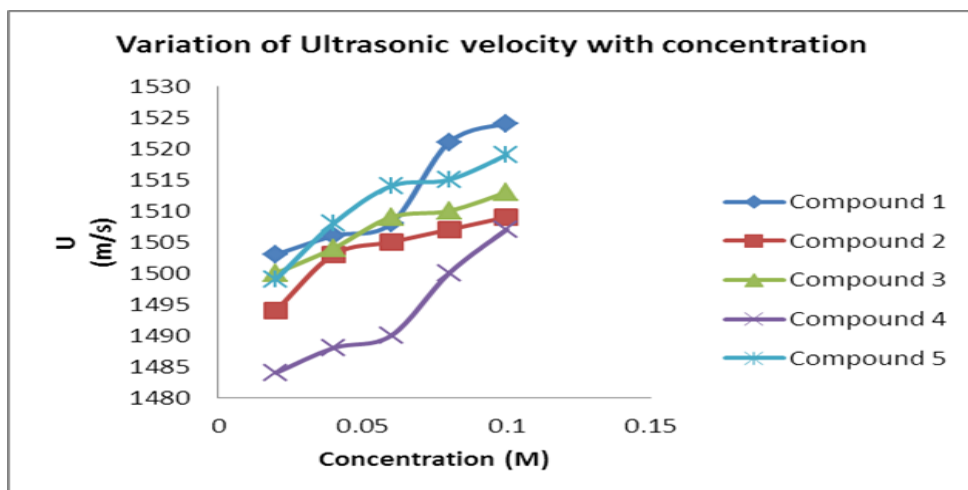


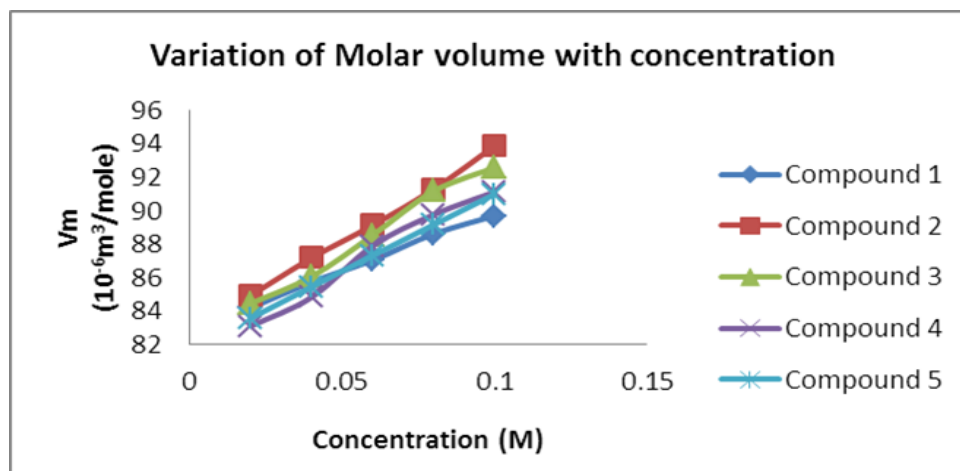
**Scheme 2.** Schematic diagram of solute- solvent interaction present in the mixture.

Figure 2 and 3 shows the linear variation of Rao's molar sound function ( $R$ ), molar compressibility ( $W$ ) with concentration whereas (Table 3). show the variation of Vander Waals constant ( $b$ ) with concentration. All the three parameters vary linearly with concentration. This linear change of these parameters suggests the absence of complex formation in these systems.

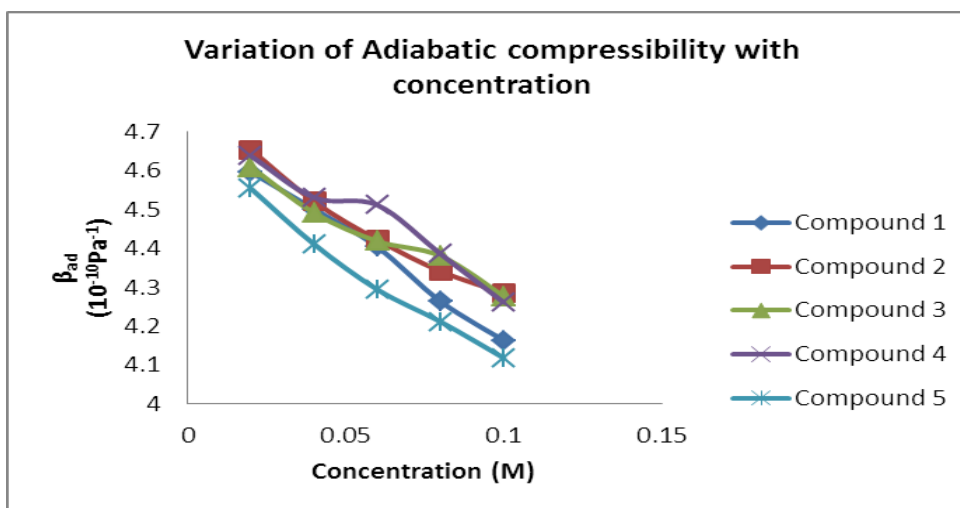
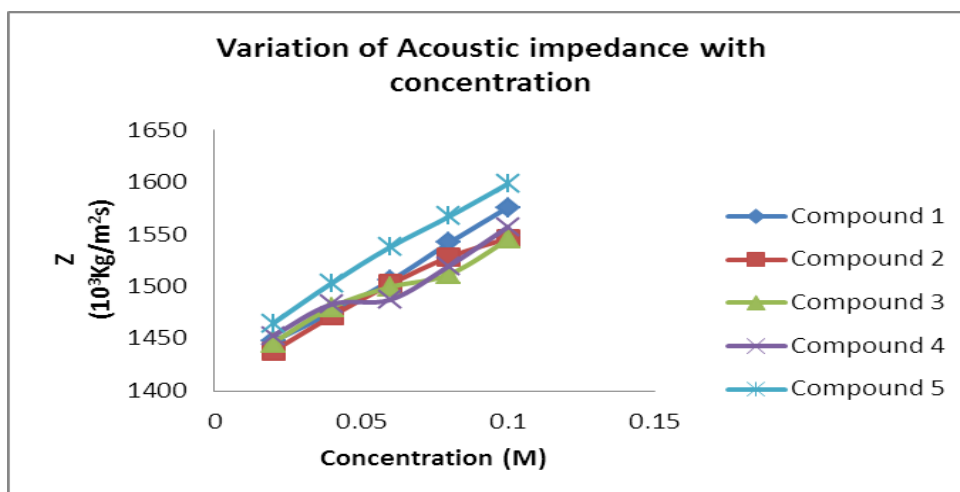
The internal pressure ( $\pi_i$ ) is the results of forces of attraction and repulsion between the molecules in a solution. Figures 5 show the variation of internal pressure with concentration for schiff base derivatives in DMSO. Although decrease in compressibility, intermolecular free length, relaxation strength and increase of velocity, viscosity suggest predominance of solute-solvent interaction, the decrease in internal pressure indicates the existence of solute-solute interactions also in these systems. It is clear from these figures that  $\pi$  decreases with concentration, which indicates the decrease in cohesive forces.

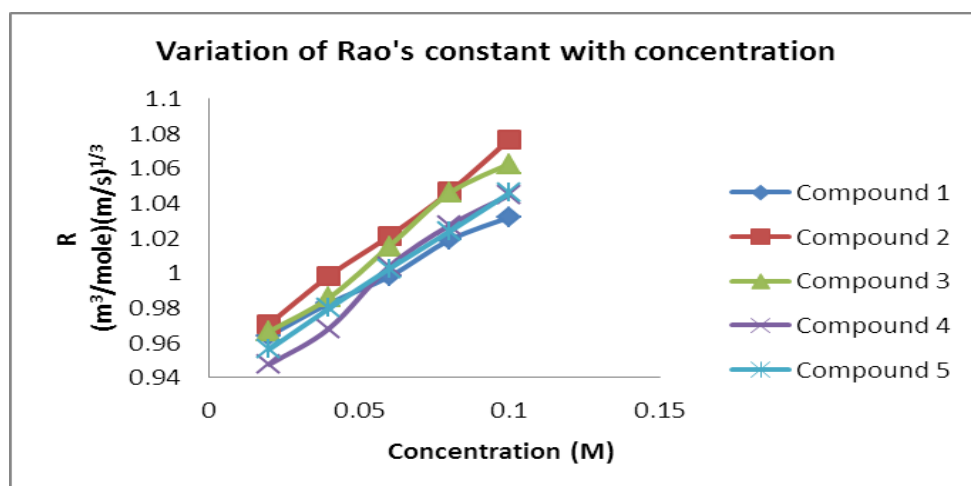
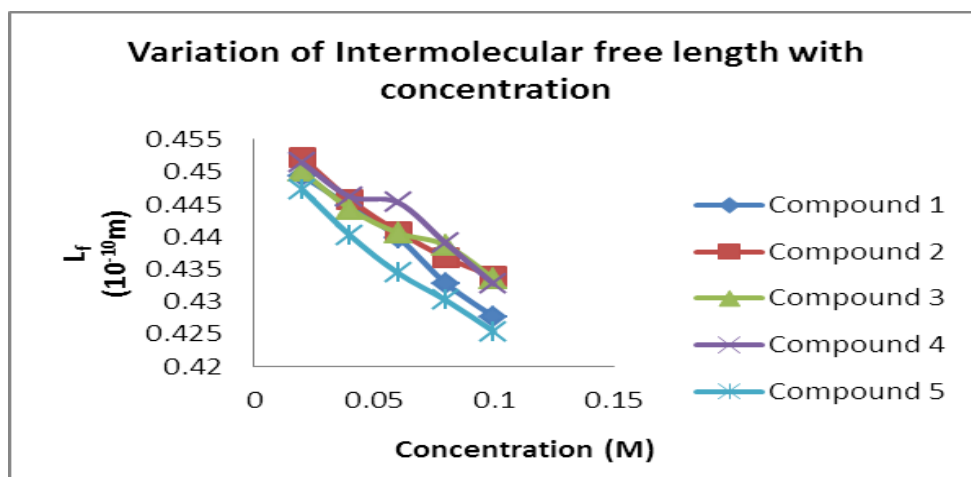
Relaxation time decreases with increase in concentration (Fig. 3). The relaxation time which is order of  $10^{-10}$  sec is due to structural relaxation [18-19] process in such a case it is suggested that molecules get rearranged due to co-operative process [20-26].



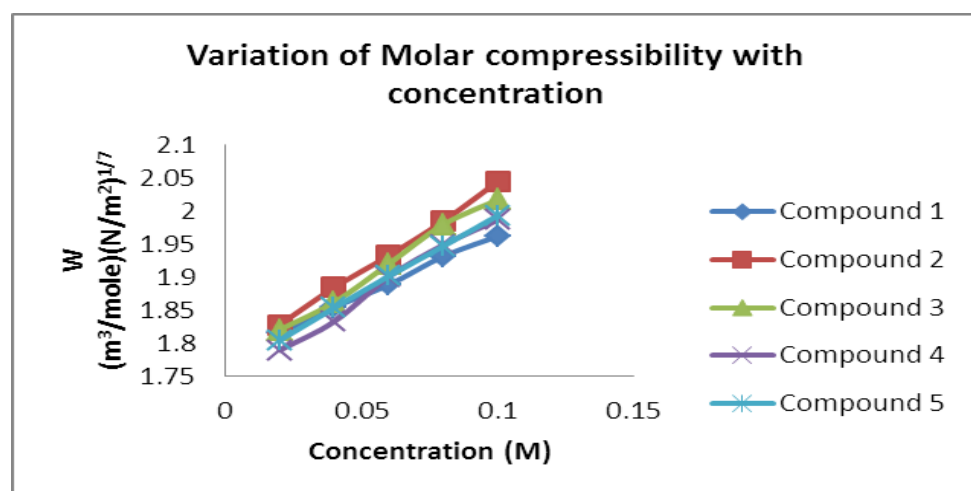


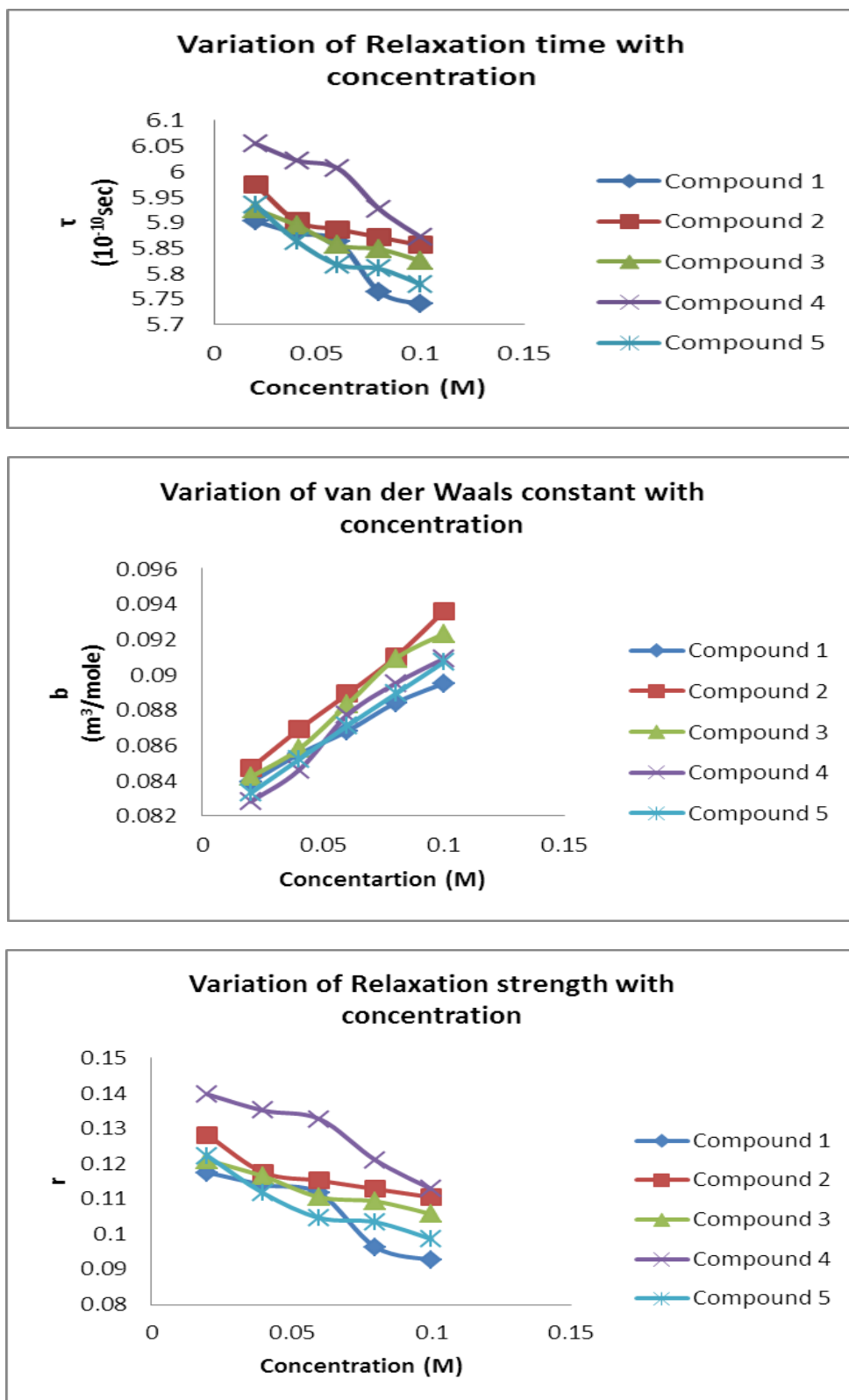
**Figure 1.** Ultrasonic velocity (U), Density ( $\rho$ ), Viscosity ( $\eta$ ) and Molar volume ( $V_m$ ) of Schiff base derivatives with DMSO at 303.15 K.



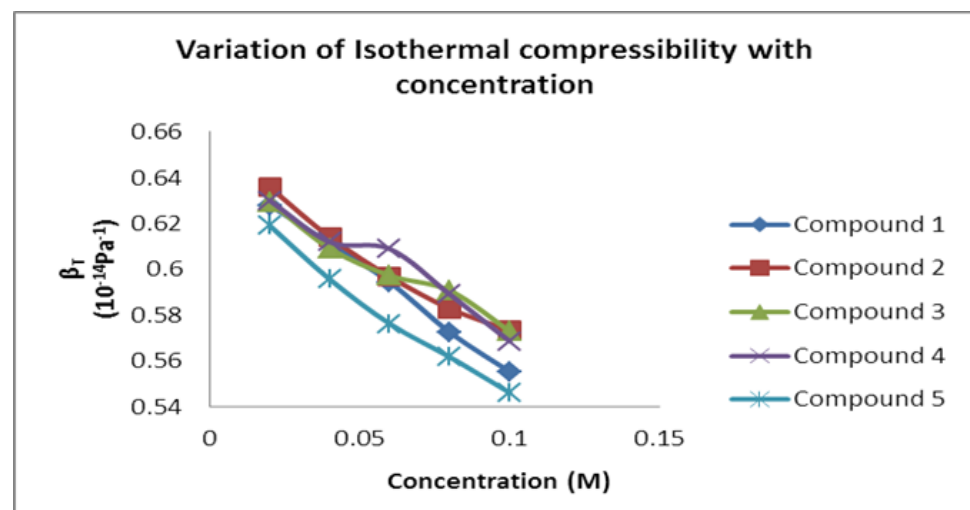
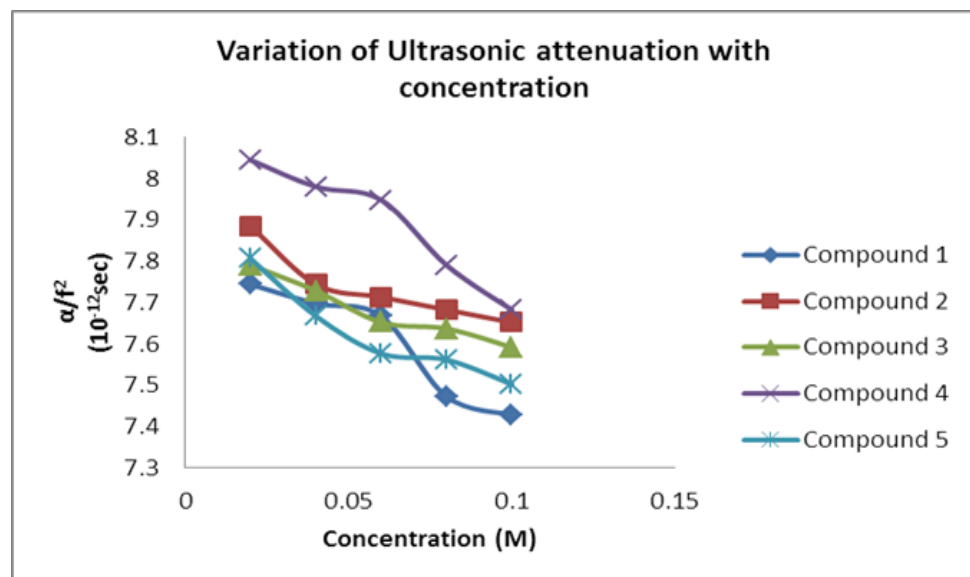
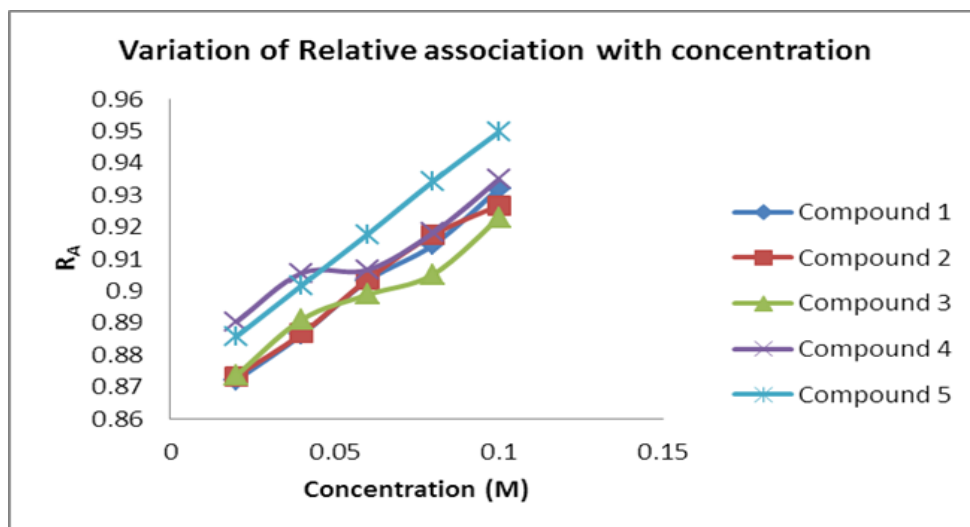


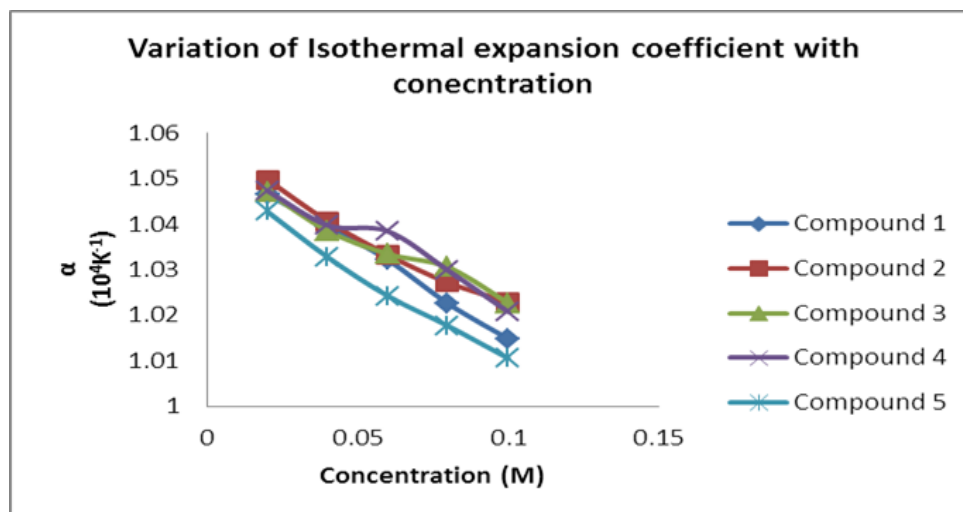
**Figure 2.** Specific Acoustic Impedance ( $Z$ ), Adiabatic compressibility ( $\beta_{ad}$ ), Intermolecular Free Length ( $L_f$ ) and Rao's Constant ( $R$ ) of Schiff base derivatives with DMSO at 303.15 K.



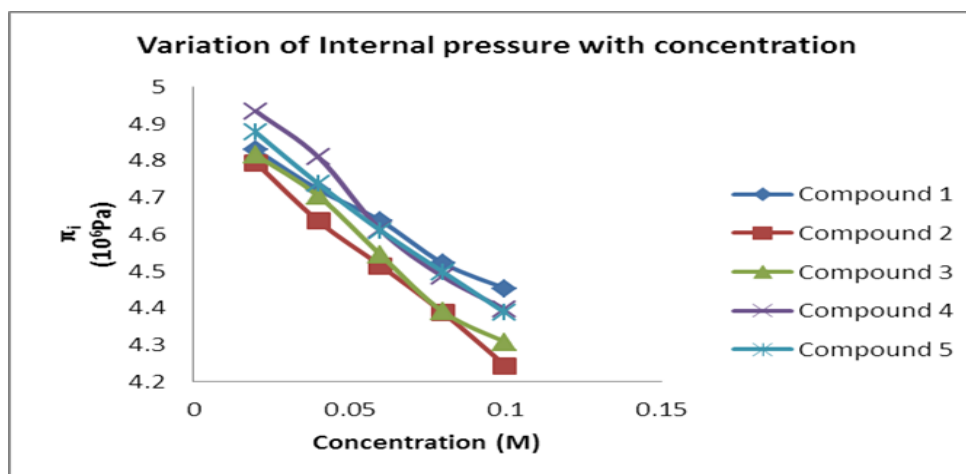
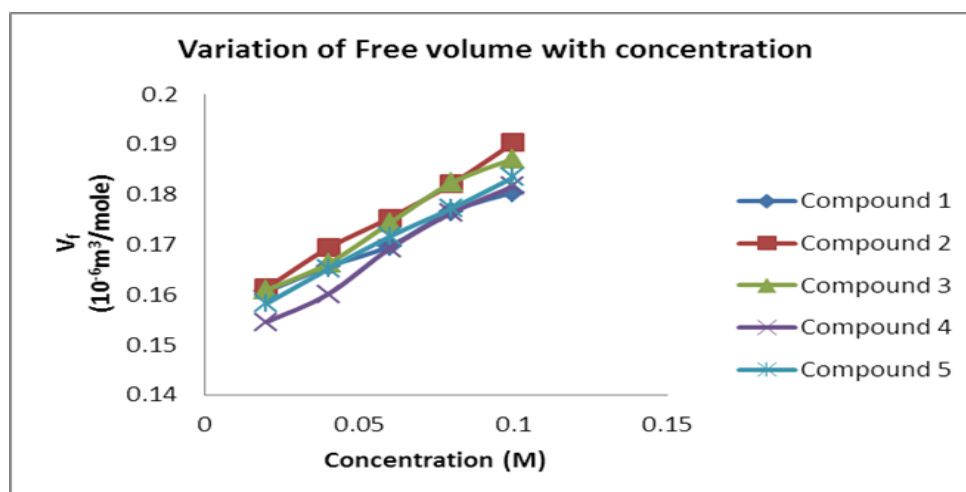


**Figure 3.** Molar compressibility ( $W$ ), Relaxation time( $\tau$ ), Vander Waals constant ( $b$ ), Relaxation strength ( $r$ ) and of Schiff base derivatives with DMSO at 303.15 K.





**Figure 4.** Relative association ( $R_A$ ) and Ultrasonic attenuation ( $\alpha/P^2$ ), Isothermal compressibility ( $\beta_T$ ) and Isothermal expansion co-efficient ( $\alpha$ ) of Schiff base derivatives with DMSO at 303.15 K.



**Figure 5.** Free volume ( $V_f$ ) and Internal pressure ( $\pi_i$ ) of Schiff base derivatives with DMSO at 303.15 K.

The free volume of solute molecule at particular temperature and pressure depends on the internal pressure of liquid, in which it was dissolved (Fig. 5) shows the variation of free volume with concentration for all the compounds in DMSO. The decrease in molecular association causes an increase in free volume. Thus, free volume is an inverse function of internal pressure. It is evident from (Fig. 5) that free volume increases with concentration for all the compounds, indicating the presence of solute-solute interactions also. This suggests that both solute-solute and solute-solvent interactions exist in these systems

#### **4. CONCLUSION**

Further, as these systems are characterized by hydrogen bonding, the solute-solvent interactions can be interpreted in terms of structural change that arises due hydrogen bond interactions between various components of the solvent solution systems. DMSO belong to the solvent having functional group of S=O, While Schiff base derivatives belong to solute having functional group CH=N and aromatic ring containing substituent. Thus, the overall finding suggests that the studied compounds exhibit solute-solvent interactions i.e. structure forming tendency of these compounds in DMSO solvent.

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