Acoustic parameter investigation of tyrosine derivative in Dimethyl Sulphoxide (DMSO) by Ultrasonic Technique

A

Dissertation-II report submitted by

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TO

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In

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Under the guidance of

Dr. K.C. Juglan (Supervisor)

Dr. Ajay Sharma (co-supervisor)

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CERTIFICATE

This is to certify that Suman Kumari has completed M.Sc. (Hons.) Physics Dissertation titled "**acoustic parameter investigation of tyrosine derivative with dimethyl sulpho oxide by ultrasonic technique**" under my guidance and supervision. To the best of my knowledge, the present work is the result of her original investigation and study. No part of work has ever been submitted for any other degree or diploma at any university except in the Lovely Professional University.

The dissertation is fit for the submission and the partial fulfillment of the condition for the award of degree of M.Sc. (Hons.) Physics.

Date:

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DECLARATION

I Suman Kumari daughter of Mr. Baldev Singh do hereby declare and affirm that the dissertation on the topic **"Acoustic parameter investigation of Dipeptide (tyrosine derivative) in Dimethyl Sulpho oxide by ultrasonic technique** done for the degree of M.Sc. (Hons.) Physics is authentic and my original work. The work done have been not submitted for any publication at any other university or institute except at Lovely Professional University.

Date

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AKNOWLEDGEMENTS

Through this column, I would like to express my heartfelt gratitude to Dr. Kailash Chandra Juglan, HOD, department of physics, School of Sciences, Lovely Professional University for supervising and guiding me in dissertation work. Without your sincerity and words of encouragement, my dissertation will not success one.

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Last but not least I would like to thank, God, my family and friends for staying with me during my dissertation work and special thanks to Lovely Professional University for providing me such an opportunity to be the part of this work.

SUMAN KUMARI

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SYMBOLS:

U- Ultrasonic velocity

ρ- Density

η- Viscosity

β- Adiabatic compressibility

L_f – intermolecular free length

V-Free volume

Z- Acoustic impedance

b- Vander Waal's constant

R- Rao's constant

W- Wada's constant

α/f^2- Ultrasonic attenuation

X_1- Mole fraction of solute

X_2- Mole fraction of solvent

W_1-Weight of distilled water

W_2-Weight of experimental liquid

M_{eff}- Effective molecular weight

r- Relaxation strength

π- Internal pressure

t_1 -Time of flow of water

t_2 - Time of flow of experimental liquid

ABSTRACT

In the present study Tyrosine derivative with non-aqueous (DMSO) solution is taken as the sample and the fundamental parameters, namely density (ρ), viscosity (η) and ultrasonic velocity (U) are determined for different concentrations at a temperature of 290K. Using these fundamental parameters acoustic and thermodynamic parameters, i.e. intermolecular free length, relaxation time, acoustic impedance, adiabatic compressibility, Rao's constant, Wada's constant, free volume, available volume, internal pressure, Vander Waal's constant, relative strength, ultrasonic attenuation and Gibb's Free energy are computed and analyzed. The non-linear variations obtained from these parameters suggest a weak interaction among tyrosine derivative and Dimethyl Sulphoxide.

Chapter 1

1.1 Introduction:

Ultrasonic is the universally accepted technique to study the physiochemical properties of the liquids, liquid mixtures, electrolytic solutions and polymeric solutions. These solutions find wide applications in medical, pharmaceutical, chemical, leather, textile and solvent- solution related industries. The study and understanding of the thermodynamic properties of liquid mixtures and solutions are more essential for their applications in these industries. The measurements of ultrasonic velocity in the combination of density and viscosity have been used to study the molecular interactions in liquid mixtures and solutions.[12]

Proteins are the linear macromolecules consisting of one or more chains of amino acid residue and having a very complex structure. There are nearly about 20 amino acids which are building blocks of living organisms. Due to the complex nature of proteins, direct study is not easily possible[15]. So by studying the nature of amino acids and peptides; we can gain a large amount of information regarding proteins. Ultrasonic study of amino acids in aqueous solution of electrolytes or non- electrolytes provides useful information related to behavior of media.[9] Electric field of the ion affects the stability of proteins.

The variation of ultrasonic velocity with concentration shows extent of interaction between solute and solvent. Ultrasonic propagation parameter yields valuable information regarding the behavior of liquid system, because intermolecular and intra-molecular association, dipole interactions, complex formation and related structural changes affect the compressibility of liquid which produces variation in ultrasonic velocity.[23]

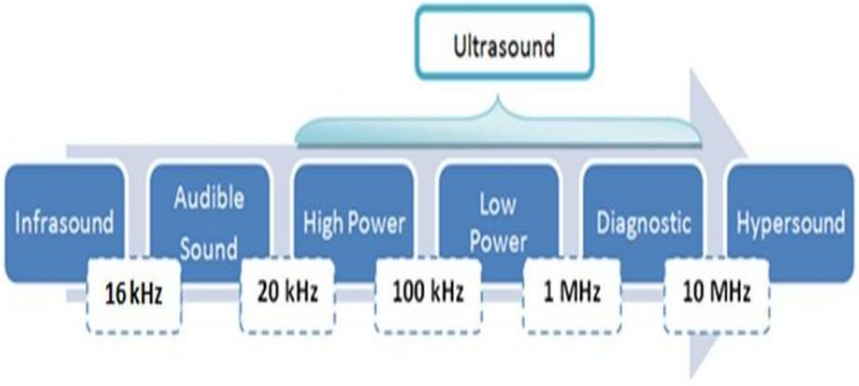
Internal pressure is measure of attractive and repulsive forces between the molecules. The internal pressure of hydrogen bonded liquids is large as compared to non-hydrogen bonded liquids.[2] Free volume is the free space available between the molecules. Free volume and internal pressure show opposite behavior.

1.2 Ultrasonic:

Ultrasonic is the science of acoustics dealing with the generation and use of inaudible acoustic waves. The sound waves having frequencies range above 20KHZ i.e. human audible ranges are called ultrasonic waves. The sound waves of low frequencies, i.e. below the human audible range are infrasonic waves. Like life, ultrasound was originated from the sea. The five senses of living beings, i.e. hearing, touch, smell, sight and taste are interdependent on each other. Out of these five, two are important for long range interaction, i.e. sight and hearing and another three have short range performance. But these things are different under water because long range sight has no use under water. By default, sound waves have long range sensing functionality under water.

The era of ultrasonic began with the wrecking of RMS Titanic, which was crushed with icebergs. The detection of the iceberg was done by high frequency waves. In 1915 Langevin (the father of ultrasonic) invented the underwater SONAR for submarine detection. Sokolov suggested the concept of ultrasonic metal flaw detection in 1928. After that slow and steady progress was made in the measurement of the propagation constant of the material. The propagation of ultrasonic waves through solid material has been used to detect hidden cracks, porosity, voids and other discontinuities in metal. The field of ultrasonic has wide application in science, medicine and defense.

The frequency range of ultrasound



1.3 Broad areas of ultrasound:

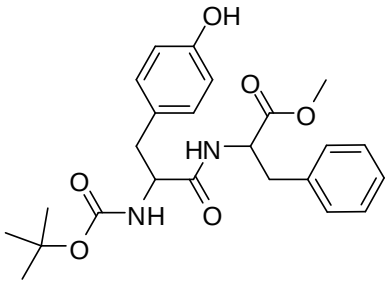
The ultrasound can be further subdivided into distinct region's power and diagnostic. The extended range of diagnostic ultrasound lies in between 5MHZ to 10 MHZ and the range of powerful diagnostic is order of low frequency i.e. 20KHZ to 2MHZ. The ultrasound does not interact directly with the molecules to induce chemical change.

Ultrasonic is a non-destructive technique used for detecting microscopic discontinuities in the structure. This technique is based on the principle of reflection of sound from interfaces between two different materials. Due to the capability of ultrasonic technique for the estimation of the orientation, shape, size and nature of defects; it is used widely in the industry. The commonly used NDT techniques are magnetic particle, liquid penetrant, radiographic, ultrasonic and eddy-current testing. A single NDT technique cannot give information regarding flaw detection or measurement applications. Each technique has advantages and disadvantages over other technique. The advantages of the NDT ultrasonic technique are

- This technique is nonhazardous to operator and material.
- It is very accurate method in determining the reflector position and estimating size and shape.
- It is sensitive to both surface and surface discontinuities.
- Minimum part preparation is required.
- It is cost effective technique.
- The frequencies associated with relaxation phenomena fall within the range of ultrasonic therefore can be easily focused.

In the ultrasonic testing, high frequency sound waves are sent into a material by the transducer. The sound waves travel through the material with some attenuation and also reflected at interfaces. The reflected or transmitted wave signal is converted into an electrical signal by same transducer. The reflected or transmitted wave signal is analyzed to determine the presence, size, location of flaws, wavelength and discontinuities.

1.4 Structure of the tyrosine derivative (dipeptide): Peptide bond is formed when two amino acids combine and water is removed, i.e. H from first amino acid and OH group from the second amino acid. When three amino acids combine through two peptide bonds, then dipeptide is formed.



Chapter 2

2.1 REVIEW OF LITERTURE:

Jacobson et al., (1952) studied the relation between adiabatic compressibility and isothermal compressibility as a function of the intermolecular free length of liquids at 20^0C. It was observed that the intermolecular free length can be obtained from available volume and internal surface of liquid.[6]

Yadava (1995) studied molecular interactions between binary mixtures with the help of molar volume, density and viscosity measurements. The existence of different type of interaction is discussed on mixing of solvent. The magnitude of different type of forces depends upon the type of solvent used. [24]

Mekawy et al., (2005) used various methods for viscosity measurements like ultrasonic pulse echo method, co-axial cylinder method, glass Viscometer. The results were compared with glass Viscometer. The experiment was performed over ten oil samples. The viscosities measured by three methods are in good correlation and can be applied industrially. The pulse echo method has advantages of its in destructive nature along with ease of operation. [8]

Krzysztof Bebek, et al., (2006) this paper is based on the Schaaffs theory of ultrasonic speed in organic liquids. The physical parameter with space –filling ability and molecular radius were derived and analyzed. The ultrasonic velocity and experimental density has used to calculate adiabatic and isothermal compressibility coefficients, molar volumes, molar isochoric heat capacities and Beyer's parameter of nonlinearity and mean molecular radius for the binaries.[8]

Several et al., (2007) studied acoustic techniques that have been applied to the food industry. Cow's milk is a major source of essential nutrients for adults and children. Spectroscopic, chromatography and enzymatic methods are used to monitor the quality of milk. Acoustic techniques are simpler than these methods. Speeds of sound and densities of milk + $NaHCO_3$ and milk + H_2O_2 at different temperatures have been measured. From densities and speeds of sound, specific acoustic impedance has calculated. Acoustic properties are very suitable for detecting chemical additives in milk.[17]

P. Vasantharani et al., (2009) studied the ultrasonic velocity together with density and viscosity data furnish a wealth of information about the interaction between ions, dipoles, hydrogen bonding, multipolar and dispersive forces.[13]

S. Trimaran et al., (2009) studied the ultrasonic velocity, density and viscosity measurements for four amino acids, namely L-alanine, L-leucine, L-Valine and L-proline in aqueous sodium acetate solution as a function of composition at 303K, 308K and 313K. Experimental data have been used to estimate the adiabatic compressibility, change in adiabatic molar volume, limiting apparent molar volume and constants and viscosity B-coefficients. The results are discussed in terms of structure-making or structure breaking effects of amino acids in the mixture.[16]

S. Ravichandran et al., (2010) Acoustic parameters of Zinc sulfate and Zinc nitrate in distilled water at 303K has been calculated. These parameters have calculated experimentally with Ultrasonic interferometer, Pycknometer, Ostwald Viscometer and compared with theoretical values using Nomoto's relation, free length theory, impedance dependent relation. Small deviations have been among experimental and theoretical values. The variation in ultrasonic confirmed the presence of strong ion-dipole interactions.[18]

Shilpa Mirikar et al., (2010) acoustic parameters: ultrasonic velocity, density and viscosity have been measured for glycine in double distilled water at different temperatures. For studying the interactions between the system acoustic and thermodynamic parameters have been computed. The nature of variation of these parameters with concentration and temperature indicates the strength of interactions in the system.[22]

C. Shanmuga Priya et al., (2010) Ultrasonic velocity, density and viscosity has been measured for binary liquid mixtures containing Methylacrylate+2-Ethoxy ethanol, Methyl methacrylate+2-Butoxy ethanol at 303K. Acoustic and volumetric parameters are used to discuss the molecular interactions in the mixtures. The free length, free volume, internal pressure, relaxation time, acoustic impedance and Gibb's free energy values have been calculated from the experimental data.[4]

R. Palani et al., (2011) studied density, ultrasonic velocity of L-Histidine, L-arginine and L-lysine in aqueous sucrose at 298,303 and 308K. Using the experimental

values viz. adiabatic compressibility, hydration number, apparent molal compressibility, apparent molal volume, limiting apparent molal compressibility, limiting the apparent molal volume and viscosity B coefficients of Jones-Dole equation. These parameters were used to study the ion-solvent interactions present in each solution.[14]

Prinyka Tabhane et al. (2012) Ultrasonic velocities, densities and viscosities have been measured in 0.1M solution using pulse echo overlap technique at 293K at different concentrations of polyvinyl chloride in tetrahydrofuran. Thermo acoustical parameters viz., adiabatic compressibility, relaxation time, molar sound velocity, molar compressibility, acoustic impedance, Vander Waals' constant and internal pressure have been computed from the experimental data. The variation of ultrasonic velocity and other thermo-acoustical parameters shows a nonlinear increase or decrease with molar concentration. [11]

E. Jasmine et al. (2012) studied solute solvent interactions are conveniently with application of acoustic and spectroscopy techniques. Measurement of sound velocity is having an important role in the study of thermodynamic properties such as internal pressure, free volume of solution. In the present study L. Arginine derivative with non-aqueous solution is taken as the sample and the fundamental parameters, namely density, viscosity and ultrasonic velocity are determined for different concentrations from very low temperature to a higher temperature. Using these fundamental quantities acoustic and thermodynamic parameters is computed and analyzed. [5]

Shipra Baluja et al., (2012) Density, viscosity and ultrasonic velocity of imidazolinone derivative have been observed in dimethyl Sulphoxide (DMSO) at 308.15K over a wide range of concentrations. The various acoustic parameters such as acoustic impedance, isentropic compressibility, relaxation time, Rao's molar sound function, internal pressure and relative association has been calculated from experimental data and it is observed that both solutes-solvent and solute-solvent interactions exist in the solution. [19]

S. R. Kanhekar (2012) ultrasonic velocities, densities and viscosities have been measured for the binary liquid mixtures. With the help of fundamental parameters adiabatic compressibility, intermolecular free length, acoustic impedance and relative association have been computed using standard formula. Increase in ultrasonic velocity

and decrease in adiabatic compressibility with a rise in concentration in both binary mixture shows the presence of complex formation and coordinate covalent bond between the molecules of mixtures.[21]

Baljinder Kaur et al., (2013) Acoustic parameters of polyvinyl acetate with acetic acid have been measured for different concentrations at 299K. Ultrasonic velocities for the binary mixture at 1MHZ and 2MHZ have been calculated and from fundamental parameters various parameters like adiabatic compressibility, acoustic impedance, intermolecular free length, ultrasonic attenuation and relaxation time has been calculated. The variations in parameters indicate the presence of strong molecular interactions between the molecules of mixture. The variations in Rao's and Wada's constant indicate absence of complex formation.[3]

Chapter 3

3.1 Scope of study:

Dipeptide acts as an inhibitor for diabetes. In the present study, the weak interaction shows emphasizing the fact that the inhibitor should bind strongly with the enzyme involved in the diabetes rather than DMSO. DMSO is used as a solvent in INVITRO study.

3.2 Objective:

To investigate acoustical parameters: ultrasonic velocity, density and viscosity and plenty other parameters of tyrosine derivative in the Dimethyl Sulphoxide (DMSO) at different concentrations.

3.3 Research methodology:

A solution of dipeptide having molecular weight 442gms in DMSO was prepared at different concentrations at constant temperature of 290K. The fundamental parameters: ultrasonic velocity, density and viscosity were calculated with ultrasonic interferometer (Mittal Enterprises F-80 Model) at the standard frequency of 2MHZ, specific gravity bottle of 10ml and Oswald Viscometer respectively. With the help of these fundamental parameters other parameters: acoustic impedance, intermolecular free length, adiabatic compressibility, relaxation time, internal pressure, free volume, available volume, relative strength, Gibb's free energy, Rao's constant, Wada's constant, ultrasonic attenuation and Vander Waal's constant.

Density measurement:

The density of pure liquids and mixtures are measured by using a 10ml specific gravity bottle. The specific gravity bottle with the experimental liquid is immersed in a temperature controlled water bath. The densities of pure liquids thus obtained are found to be in good agreement with standard values. The measured density was measured using the formula,

$$\rho_2 = \frac{W2}{W1}\rho 1$$

Where,

W_1, is the weight of the distilled water

W_2 is the weight of the experimental liquid

ρ_1 is the density of water.

ρ_2 is the density of experimental liquid

Ultrasonic velocity:

Ultrasonic waves follow the relation $U = \lambda \times f$

Where, U = velocity of the wave

f = frequency of particle vibration

λ = wavelength of the wave

Viscosity measurements:

The viscosity was determined using the relation:

$$\eta 2 = \eta 1 \frac{t2}{t1} \frac{\rho 2}{\rho 1}$$

Where,

η_1 is the Viscosity of water

t_1 is the time of flow of water

ρ_1 is the density of water

η_2 is the viscosity of the experimental liquid

t_2 is the time of flow of the experimental liquid

ρ_2 is the density of the experimental liquid.

By using these basic parameters, we will calculate various parameters.

- ## Acoustic impedance (Z)

It is the resistance offered to the propagation of the ultrasonic wave in a material, and it can be defined as the product of its density (p) and acoustic velocity (U)

$$Z = \rho U$$

Acoustic impedance is important in the determination of acoustic transmission and reflection at the boundary of two materials having different acoustic impedances.

- **Adiabatic compressibility**

The adiabatic compressibility is the fractional decrease of volume per unit increase of Pressure, when no heat flows in or out. These changes are related to the compressibility of the medium by thermodynamic relation

$$\beta = \frac{1}{V}\frac{dV}{dP}$$

It can be also calculated from the speed of sound and density of the medium using equation of Newton as

$$\beta = (U^2 \rho)^{-1}$$

Where, ρ is the density of the medium

U is the ultrasonic velocity in the medium

- **Intermolecular free length**

It is the distance between surfaces of neighboring molecules and is given by the relation

$$L_f = K_T (\beta)^{1/2}$$

β, is the adiabatic compressibility of mixture

K_T, is the temperature dependent Jacobson's constant

- **Free volume**

A molecule may be treated as if it were composed of individual molecules each moving in a volume in an average potential due to its neighbors. Molecules are not closely packed and there is free space between the molecules to move. And is defined as free volume in which particular molecule of liquid can move and obey laws

$$V_f = [M_{eff}\, U / K \eta]^{3/2}$$

K – Temperature independent constant

U – Ultrasonic velocity in the medium

η- Viscosity of mixture

M_{eff} – is the effective molecular weight.

- **Relaxation time**

Relaxation time is a measure of the time taken by medium particles to revert to their original mean positions within medium following displacement by ultrasonic wave. Its value is characteristic of the medium.

Relaxation time for binary mixture can be calculated from the relation.

$$\tau = \frac{4\,\beta\eta}{3}$$

It can be also written as $\tau = \frac{4\,\eta}{3\rho U^2}$

- **Ultrasonic attenuation**

The rate of decrease of energy when an ultrasonic wave is propagating in a medium termed as attenuation and depends upon the properties of the medium.

The sound attenuation increases with an increase in the frequency and generally proportional to the square of sound frequency. So the ultrasonic attenuation can be expressed as

$$\frac{\alpha}{f^2} = \frac{8\pi^2\eta}{3\rho U^3}$$

- **Wada's constant**

Wada put forward a relation given by

$$W = (\beta)^{-1/7} M_{eff} / \rho$$

Where W is called Wada's constant or molecular adiabatic compressibility, which is independent of temperature.

- **Rao's constant**

A simple relation between the velocity of sound and the density of mixture is given by

$$R = U^{1/3} M_{eff} / \rho$$

Where U and ρ are respectively the sound velocity and density of mixture at temperature T, M is the effective molecular weight. R is a constant independent of temperature and is called Rao's constant. Rao's number gives an idea of how the nature of molecular interaction changes with concentration.

- **Internal pressure:**

The internal pressure is the cohesive force, which is a resultant of the force of attraction and the force of repulsion between the molecules. Internal pressure gives an idea about solubility characteristics. it can be calculated by using a formula

$$\Pi = bRt\,[K\eta/U]^{1/2}\,[\rho^{2/3}/M^{7/6}]$$

Where, K is a constant

T the absolute temperature

η is the viscosity

U is the ultrasonic velocity

ρ is the density of the liquid

- **Vander Waal's constant (b):-**

Vander Waal's constant is calculated by using the relation

$$b = (M/\rho).[1-(RT/MU^2)\{(1 + MU^2/3RT)^{1/2} – 1\}]$$

Where, M = molecular weight,

R = 8.3143 $JK^{-1}mol^{-1}$, is the gas constant

ρ is the density of the solution.

- **Gibb's free energy:-**

The Gibb's free energy is calculated by using the relation

$$\Delta G = KT. Ln (KT\tau/h)$$

Where, τ is the viscous relaxation time

T is the absolute temperature

h is the Planck's constant

- **Available volume ($V_{a)}$**

Available volume is calculated by using the relation

$$Va = (Vm- V_0) = Vm. [1 – U/U_\infty]$$

Where, Vm = M/ ρ , is the molar volume

U = velocity of sound in medium.

$V_0 = M/\rho_0$ = molar volume at absolute zero temperature

U_∞ = Schaaf's limiting value taken as 1600 m/s for liquids.

- **Relaxation strength (r)**

Relaxation strength was calculated by following formula

$$r = 1-[U/U\infty]$$

Where $U\infty$ = 1600m/s

Chapter 4

4.1 RESULTS AND DISCUSSIONS:

Under this sub-heading experimentally obtained values of Ultrasonic Velocity, Density and Viscosity are given. A variation of these parameters with concentration is plotted. Other Acoustical parameters like Adiabatic Compressibility, Intermolecular Free Length, Acoustic Impedance, Attenuation, Relaxation Time, Effective Molecular Mass, Free Volume, Molar Volume, Available Volume, Wada's Constant, Rao's Constant, Vander wall's Constant, Internal Pressure, Gibb's Free Energy and relaxation strength are computed with the help of standard parameters and their variation is shown in the plots with varying concentrations.

Table 4.1: Experimental values of ultrasonic velocity, density and viscosity of dipeptide in DMSO (dimethyl Sulphoxide) at different concentrations at 290K.

Concentration (%)	Ultrasonic velocity (U) (m/s)	Density(ρ) (Kg/m^3)	Viscosity (η)$\times 10^{-3}$ (Ns/m^2)
0.5	1540	1102.90	2.70
0.45	1562	1096.4	2.70
0.40	1560	1103.71	2.16
0.35	1567	1109.98	2.09
0.30	1555	1096.54	1.83
0.25	1582	1098.35	2.05
0.20	1576	1095.97	2.17
0.15	1567	1104.92	2.01
0.10	1568	1101.51	2.08

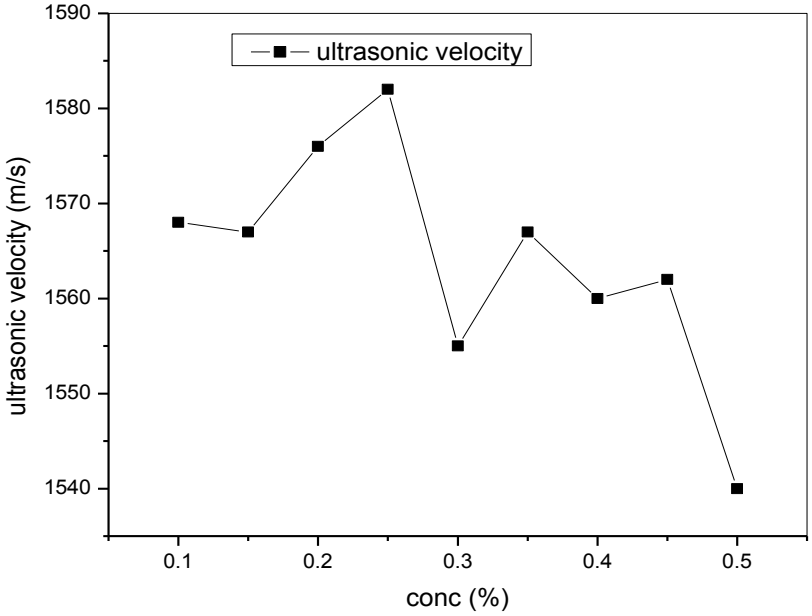


Figure 4.1: ultrasonic velocity versus concentration of DMSO at 290K.

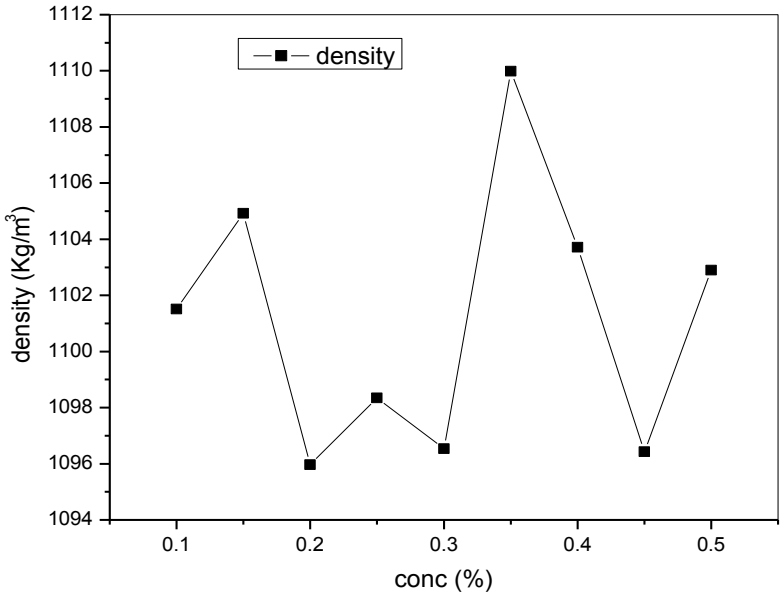


Figure 4.2: density versus concentration of DMSO at 290K

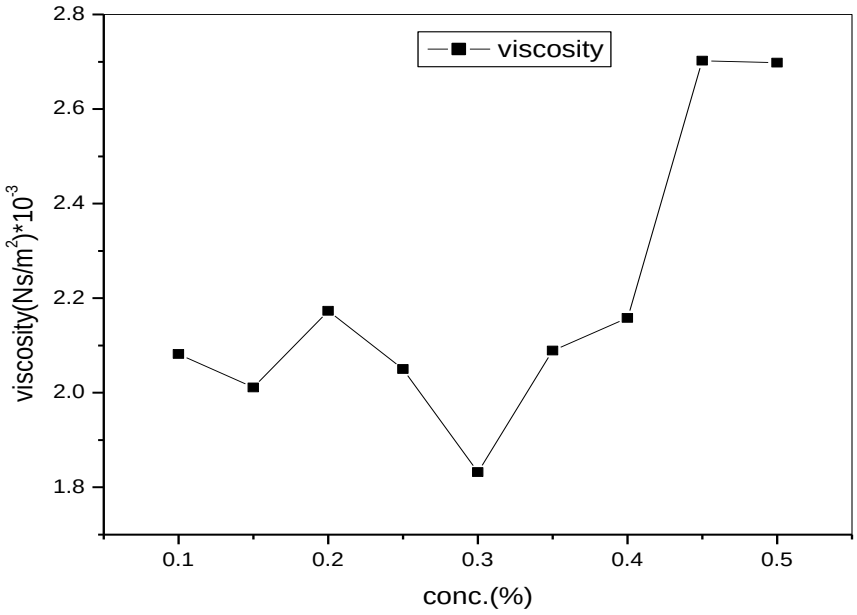


Figure 4.3: viscosity versus concentration of DMSO at temperature 290K.

Table 4.1 depicts variation of ultrasonic velocity with increase in concentration is non-linear and shows the anomalous behavior at 0.2M concentration. An initial increase in velocity with concentration in **figure 4.1** suggests an increase in cohesive forces due to powerful solute-solvent interaction. Then decrease in ultrasonic velocity after concentration 0.2M suggests breaking up of molecules of solvent when the concentration of solute is more in the solution. This suggests dissociation of molecules. This shows weak interaction between the solute and solvent.[11]

Figure 4.2 depicts the density of the mixture shows the non-linear behavior with a rise in the concentration. Density is a measure of solute-solvent and ion-solvent interactions. Departure from linearity indicates the significant solute-solvent interaction.
The viscosity of the mixture is non-linear with the increase in concentration in **figure 4.3**. This indicates that there is a significant interaction between solute and solvent. The viscosity is an important parameter in understanding the structure as well as molecular interaction occurring in the solutions. The values of viscosity increase with rise in concentration. These variations attributed to structural changes.[21]

Table 4.2: Experimental values of intermolecular free length, adiabatic compressibility, relaxation time and acoustic impedance of dipeptide in DMSO at different concentrations

Concentration (%)	Intermolecular free length (L_f) $\times A^0$	Acoustic impedance (Z) $\times 10^5$ ($Kgm^{-2}s^{-1}$)	Adiabatic compressibility(β)$\times$ 10^{-10} (m^2/N)	Relaxation time(τ) $\times 10^{-12}$s
0.5	0.499270	16.98466	3.82316	1.38
0.45	0.405344	17.12624	3.73815	1.35
0.40	0.404523	17.21788	3.72302	1.07
0.35	0.401577	17.39339	3.66899	1.02
0.30	0.407148	17.05120	3.77151	0.92
0.25	0.399869	17.37590	3.63786	0.99
0.20	0.401827	17.27249	3.67357	1.06
0.15	0.402495	17.31410	3.68579	9.88
0.10	0.402860	17.27168	3.69249	1.03

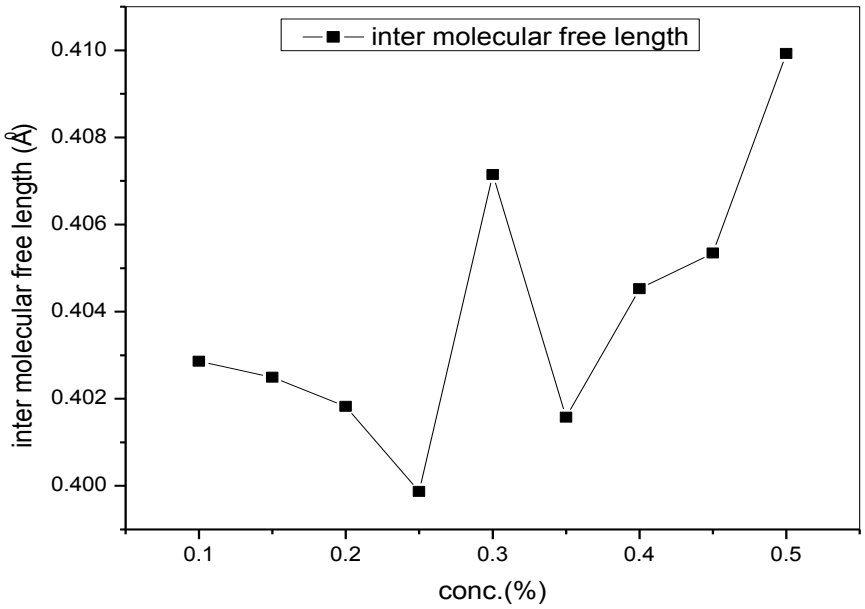


Figure 4.4: Intermolecular free length versus concentration at 290K.

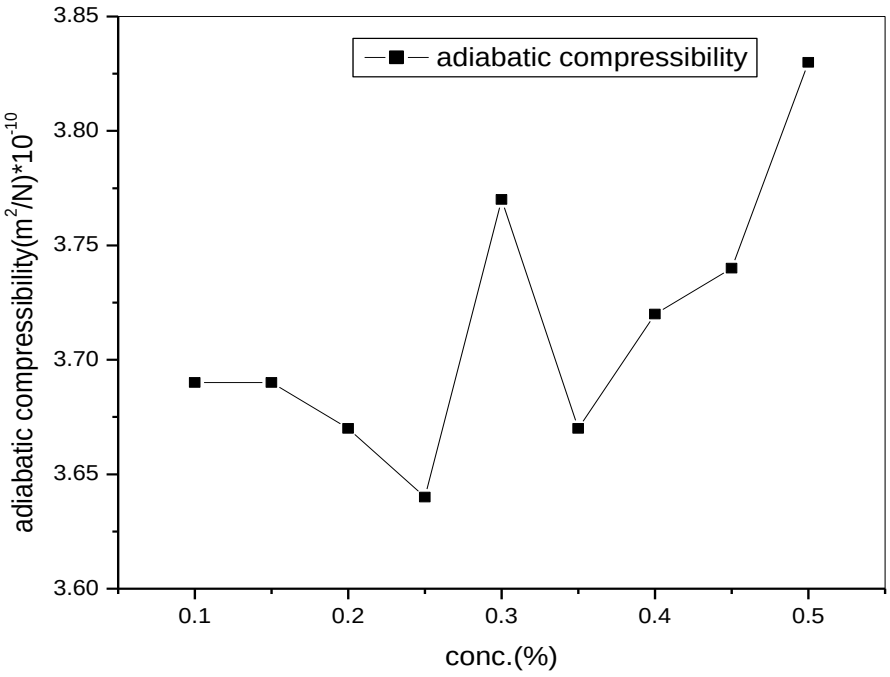


Figure 4.5: Adiabatic compressibility versus concentration at 290K.

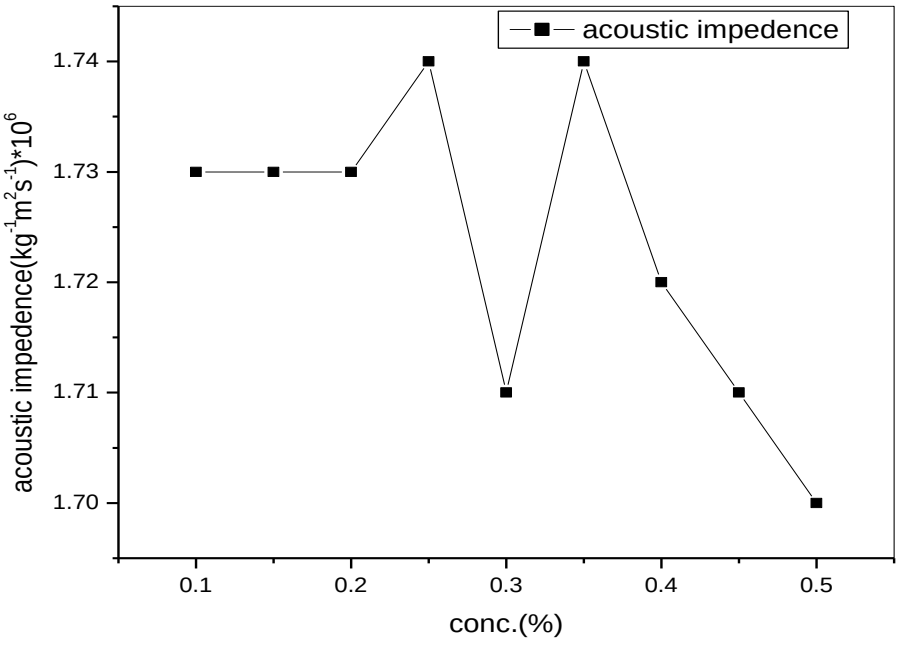


Figure 4.6: Acoustic impedance versus concentration at 290K

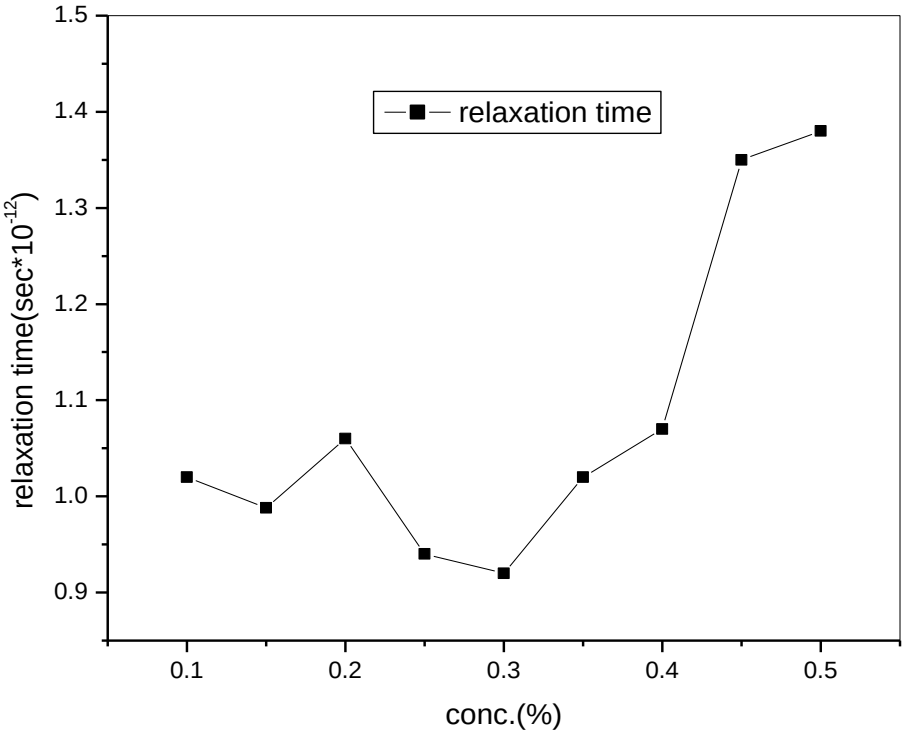


Figure 4.7: Relaxation time versus concentration at 290K.

The decrease in velocity is due to increase in free length and adiabatic compressibility of the mixture. The intermolecular free length increases with the concentration in **figure 4.4** which shows the weak interaction between the solute and solvent.

In **figure 4.5** adiabatic compressibility increases with rise in concentrations. This shows interactions among solute and solvent molecules. The structural changes of molecules in the solution take place due to the existence of electrostatic field between the interacting molecules. The arrangement of molecules results in the effect of adiabatic compressibility. Adiabatic compressibility is an indication of the change in volume that results from a change in pressure when no heat flows in or out.[5]

Relaxation time increases with increase in concentration as given in **table 4.2.** The variations in relaxation time are mainly due to the change in viscosity of solutions due to both concentration and temperature. The relaxation time is the order of 10^{-12} second is due to the structural relaxation process and such situation suggests that the

molecules get rearranged due to co-operative process. [20] This indicates the presence of specific molecular interaction among dipeptide and DMSO. The variation of relaxation time is shown in **figure 4.7.**

In **figure 4.6** acoustic impedances decrease with rise in concentrations which shows significant interaction between solute and solvent molecules.[10]

Table 4.3: Rao's constant, Wada's constant and available volume of dipeptide in DMSO at different concentration.

Concentration (%)	Rao's constant (R) $\times 10^{-4}$ $(m^3/mole)(m/s)^{1/3}$	Wada's constant (W) $\times 10^{-3}$ $(m^3/mole)(pa)^{1/7}$	Available volume $(V_A)\times 10^{-6}$ $(m^3/mole)$
0.5	7.99	1.533	2.60
0.45	8.08	1.547	1.65
0.40	8.02	1.537	1.73
0.35	7.98	1.531	1.42
0.30	8.06	1.543	1.96
0.25	8.09	1.548	0.78
0.20	8.09	1.549	1.04
0.15	8.01	1.535	1.42
0.10	8.03	1.539	1.38

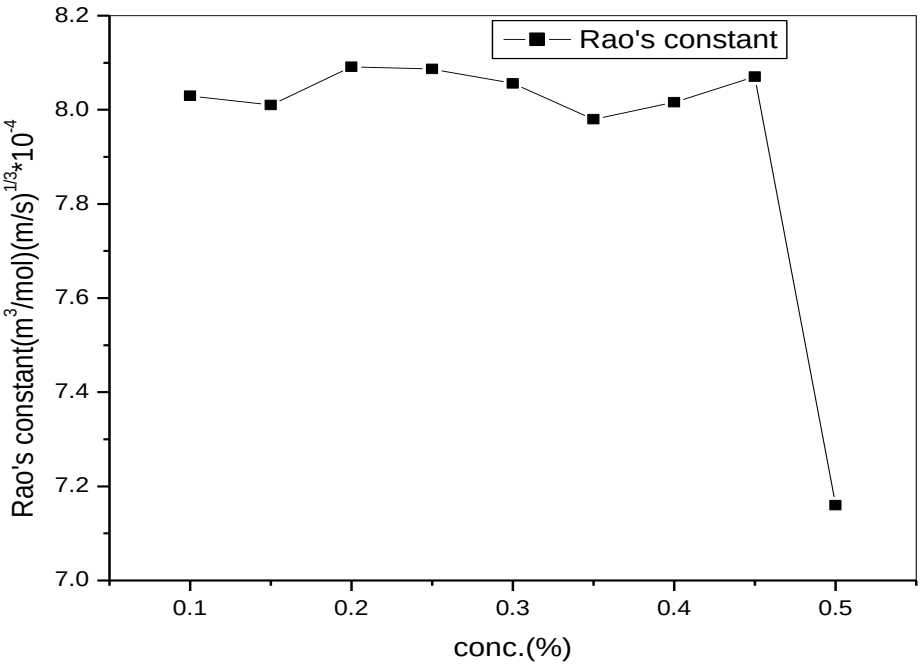


Figure 4.8: Rao's constant versus concentration at 290 K.

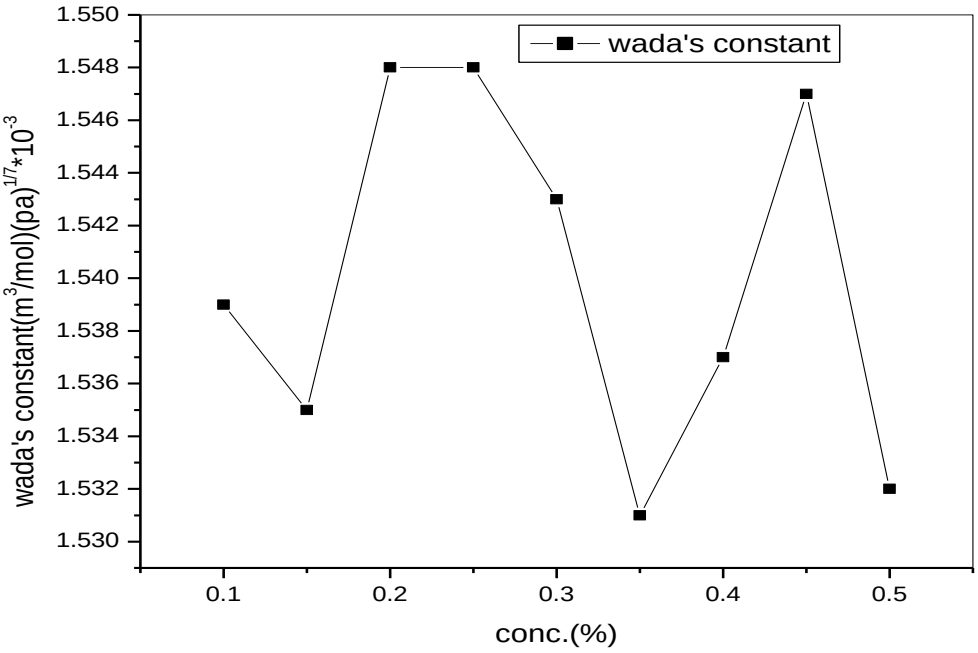


Figure 4.9: Wada's constant versus concentration at 290K.

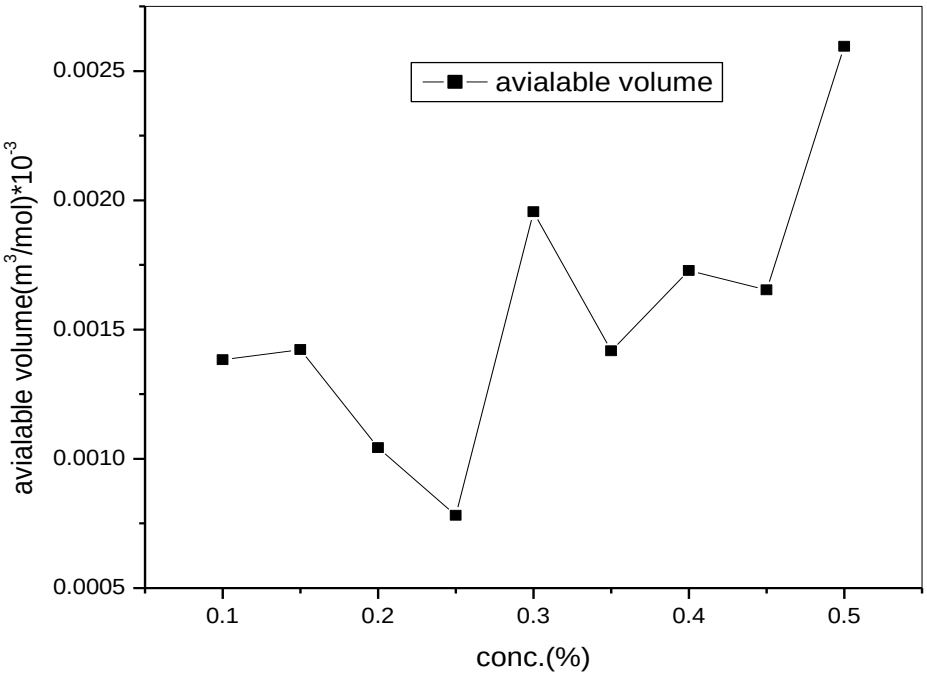


Figure 4.10: Available volume versus concentration at 290K.

In **table 4.3,** the values of Rao's constant, Wada's constant and available volume are given with varying concentrations.

Rao's constant also known as molar sound velocity shows the non-linear behavior which indicates that there is a weak interaction between solute and solvent in **figure 4.8.** Wada's constant also known as molar adiabatic compressibility may be considered for existing interaction. The values of Wada's constant decreases with increasing concentration in **figure 4.9** indicate that there must be loose packing of the medium and hence interaction is decreasing. Thus, there may be solute-solvent interaction occurring. [2] Available volume is a direct measure of the compactness and strength of bonding between the molecules of the liquid mixture. **Figure 4.10** shows, with increase in concentration of DMSO, molar volume (Vm) increases and hence Va increases.[9]

Table 4.4: Internal pressure, Gibb's free energy, ultrasonic attenuation and free volume of dipeptide in DMSO at different concentrations.

Concentration (%)	Internal pressure $(\pi)\times10^{8}$ pa	Gibb's free energy $(G)\times10^{-21}$ (KJ/mol^{-1})	Ultrasonic attenuation $(\alpha/f^{2})\times10^{-14}$ $(s^{2}m^{-1})$	Free volume $(V)\times10^{-8}$ $(m^{3}/mole)$
0.5	8.96	8.49	1.76	3.24836
0.45	8.87	8.40	1.70	3.31283
0.40	7.98	7.49	1.35	4.62527
0.35	7.86	7.30	1.29	4.88677
0.30	7.33	6.88	1.17	5.87956
0.25	7.70	7.19	1.24	5.09596
0.20	7.94	7.46	1.33	4.64014
0.15	7.70	7.17	1.24	5.16543
0.10	7.82	7.31	1.29	4.90672

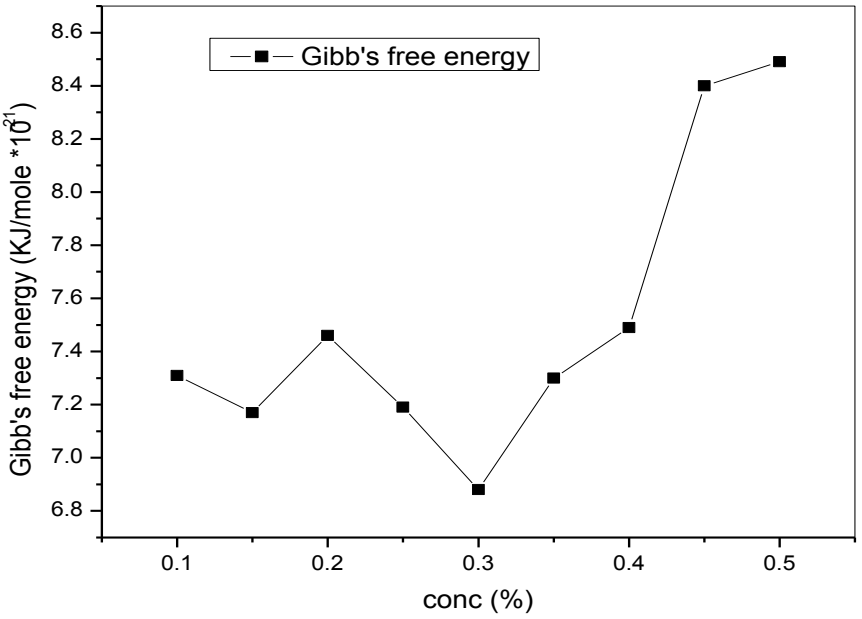


Figure 4.11: Gibb's free energy versus concentration at 290K.

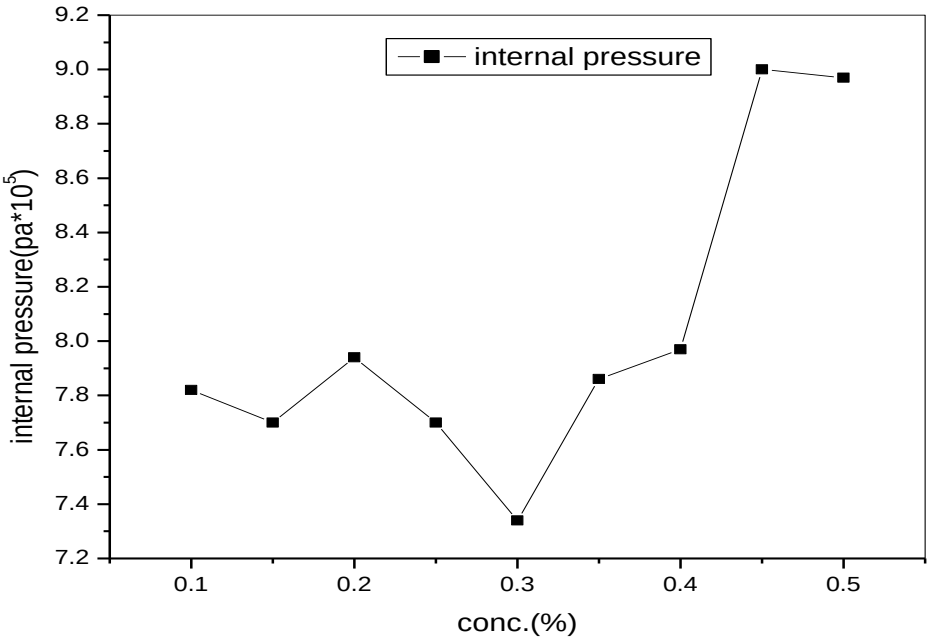


Figure 4.12: Internal pressure versus concentration at 290K.

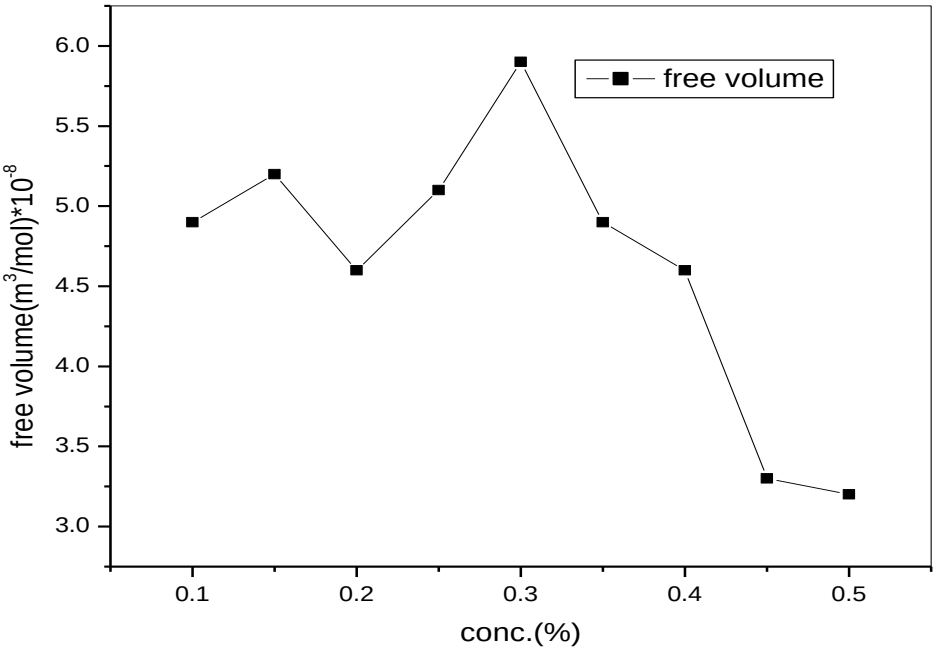


Figure 4.13: Free volume versus concentration at 290K.

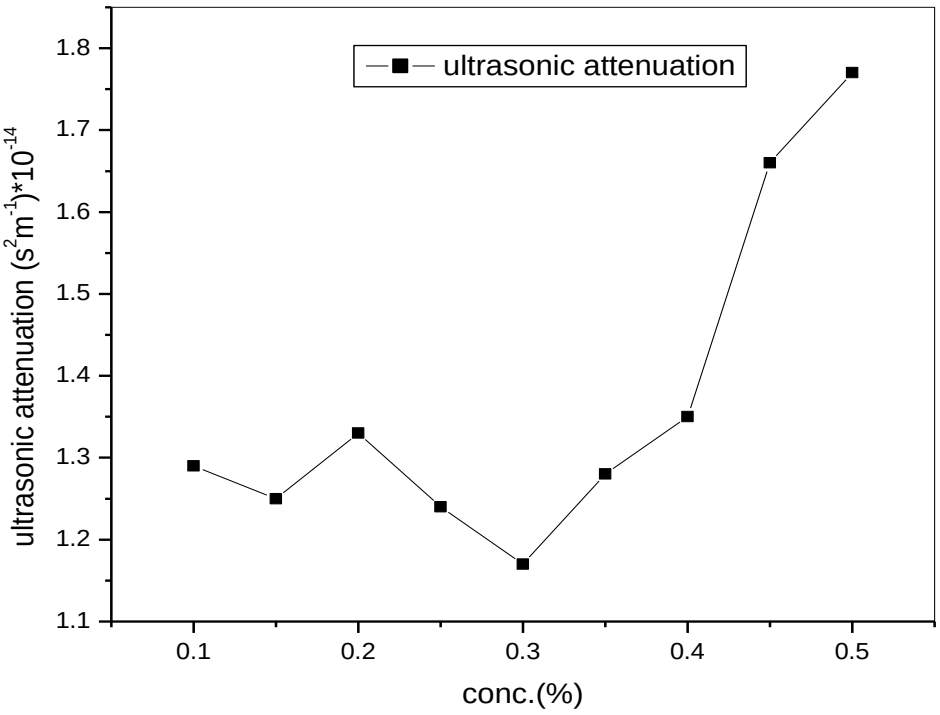


Figure 4.14: Ultrasonic attenuation versus concentration at 290K.

In **table 4.4** internal pressure, Gibb's free energy, free volume and ultrasonic attenuation are tabulated at different concentrations.

Internal pressure increases with concentration in **figure 4.12.** The free volume **(V)** is found to decrease with concentration. Ion solvent interaction is affected by two factors: (i) the breaking up of the solvent structure on the addition of solute to it and (ii) the salvation of solute. The decrease of V in **figure 4.13** (increase of π) indicates the formation of hard or tight solvation layer around the ion and increase of V (decrease of π) may be due formation of thin or loose solvation layer,[2] which shows that there is significant interactions between solute and solvent.

In **figure 4.11** Gibb's free energy increases with increase in concentrations up to 0.5M. Increase in Gibb's energy shows the rearrangement of molecules for a shorter time. It enhances the complexation.[10]

The variation of ultrasonic attenuation with concentration is shown in **figure 4.14.** Variation in the attenuation coefficient is a measure of the spatial rate of decrease in the intensity level of the ultrasonic wave. When the concentration of DMSO increases the

attenuation coefficient increases after 0.3M and the wave is more and more attenuated, which indicates the presence of weak interactions between solute and solvent molecules.

Table 1.4: Effective molecular weight, relative strength and Vander Waal's constant of dipeptide in DMSO at different concentrations.

Mole fraction of solute ($X_1 \times 10^{-4}$)	Mole fraction of solvent (X_2)	Effective molecular weight(M_{eff}) in grams	Relative strength(r)	Vander waal's constant(b)$\times 10^{-5}$ (m^3/mole)
5.71	0.9999	76.338	0.0375	6.90
4.99	0.9995	76.312	0.0237	6.94
4.33	0.9995	76.289	0.0250	6.89
3.70	0.9996	76.265	0.0206	6.85
3.10	0.9997	76.243	0.0281	6.93
2.80	0.9997	76.232	0.0112	6.92
1.97	0.9998	76.202	0.0150	6.93
1.45	0.9999	76.183	0.0206	6.87
1.05	0.9999	76.168	0.0200	6.89

In **figure 4.15** Vander Waal's constant shows non-linear behavior with rise in concentrations. The value of b increases up to 0.25M concentration and then starts decreasing, which shows the weak interaction between solute and solvent molecules. The value of molar volume varies four times the Vander Waal's constant.

Relaxation strength shows non- linear behavior with a rise in concentration in **figure 4.16** which indicates the presence of solute-solvent interaction.

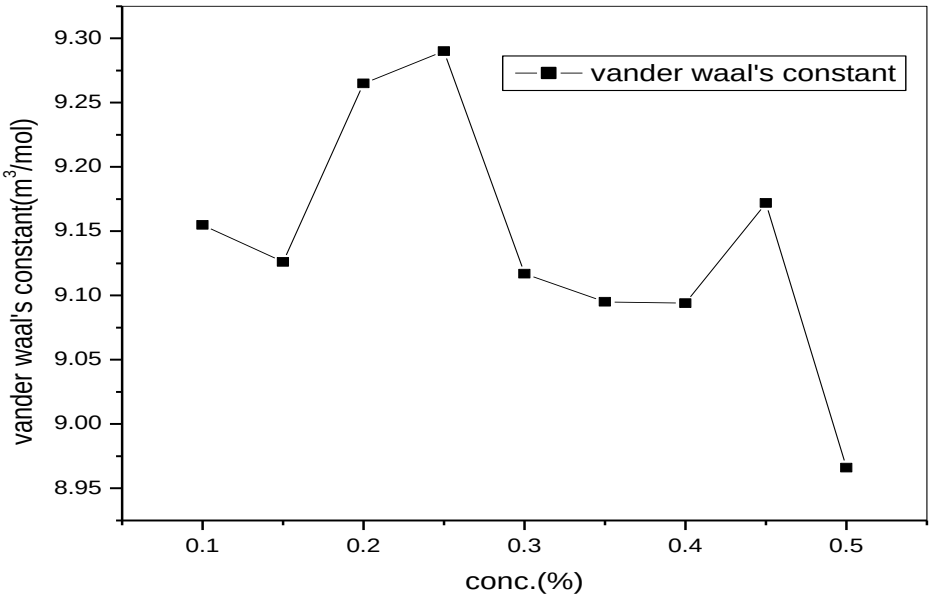


Figure 4.15: Vander Waal's constant versus concentration at 290K.

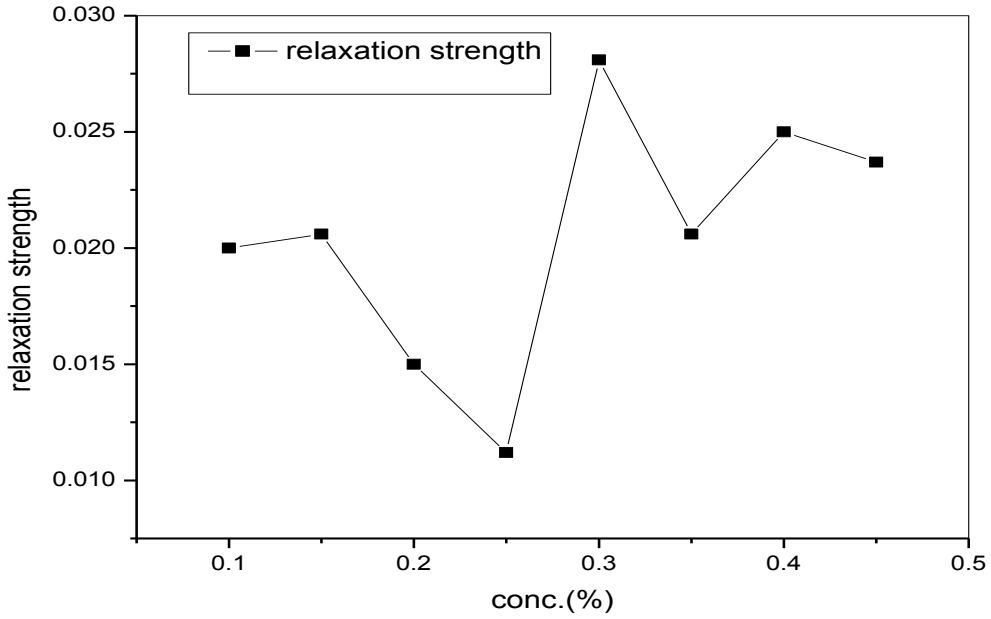
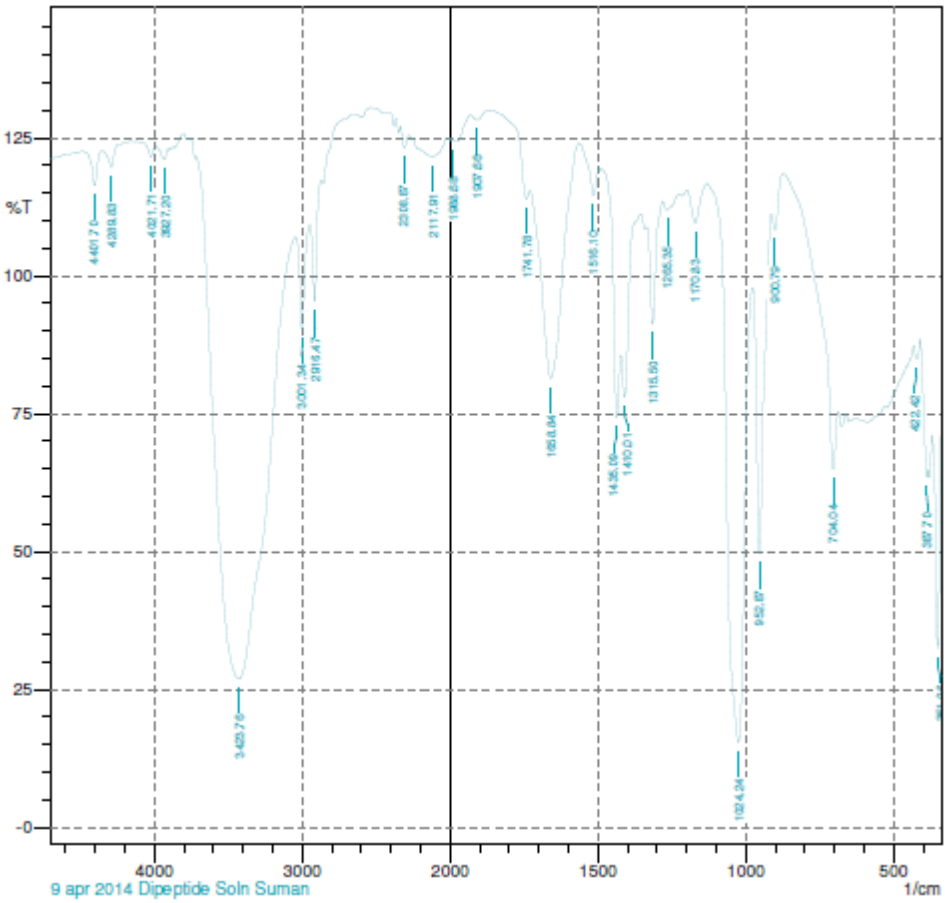


Figure 4.16: Relaxation strength versus concentration at 290K.

4.2 IR SPECTRA:

Infrared spectroscopy is the spectroscopy that deals with the infrared region of the electromagnetic spectrum i.e. light with a lower frequency and longer wavelength than visible light . It covers a range of techniques, mostly based on absorption spectroscopy. In the IR spectra of the mixture, peak 3423.76 cm^{-1} indicates the presence of O-H group attached to benzene ring. In the benzene ring all C atoms are sp^2 hybridized and peak 1658.84cm^{-1} depicts the presence of carbon-carbon double bond. Carbonyl group C=O is attached to nitrogen atom which is electronegative in nature withdraw the electrons of carbon and makes it electron deficient. The lone pair of the oxygen shifts towards the carbon to make it electron rich and peak 1741cm^{-1} shows the presence of C=O group. Peak 1024cm^{-1} depicts the presence of Sulphoxide group. C-C stretching in the methyl group is shown by 1315cm^{-1} peak.



IR spectra of the mixture

4.3 CONCLUSION:

In the present study of tyrosine derivative in dimethyl sulpho oxide we have observed that the ultrasonic velocity decreases with the rise in concentration. Adiabatic compressibility, intermolecular free length and relaxation time show the opposite behavior to ultrasonic velocity. Internal pressure increases with the concentration and free volume decreases with the concentration. The variation of Rao's and Wada's constant with the concentration is non-linear. Decrease in Vander's Waal's constant with the concentration is an indication of weak interaction. The variation of acoustic and thermodynamic parameters with different concentrations indicates that there is a weak interaction between the solute and solvent molecules in the solution.

Chapter 5

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