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The Study of Propagation of Ultrasonic Waves and Molecular Interactions in the Solutions of Magnesium Salicylate Tetrahydrate

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Abstract: Present study deals about the experimental results of ultrasonic velocity, density and viscosity along with estimated parameters for the liquid mixture of magnesium salicylate tetrahydrate (MST) as solute and 50% ethanol as a solvent at 298.15K, 303.15K and 308.15K temperatures. The frequency selected for measurements of velocity is 4MHz. The measured values of density (ρ), ultrasonic velocity (v) and viscosity (η) are used to calculate various thermoacoustic parameters like Adiabatic compressibility (β_s), free length (L_f), Specific acoustic impedance (Z), Apparent molar compressibility (ϕ_K), free volume (V_f), Relaxation time (t), Relative association (R_A), Rao's constant (R) and Wada's constant (W). The calculated values are utilized to study the intermolecular interactions existed between magnesium salicylate tetrahydrate in 50% ethanol. The variation in the values of these parameters with composition of the mixture at the temperatures 298.15K, 303.15K and 308.15K has been discussed in terms of molecular interaction between the components of liquid mixtures.

Keywords: Ultrasonic Velocity, Viscosity, Free Volume, Acoustic Impedance, Raos Constant, Molecular Interactions.

I. INTRODUCTION

Ultrasonic velocity measurement and calculation of associated parameters is one of the key factors to study the nature of liquid mixture. Ultrasonic wave propagation in liquid has been the subjects of exhaustive research which has been carried out theoretically and practically. The number of techniques are used to study the molecular structures in mixtures. Ultrasonic methods have the added advantage of being less cost with efficiency comparable to other methods. Many researchers have used ultrasound to study the molecular interactions in aqueous solutions containing electrolytes [1].

Ultrasonic wave propagation affects the physical properties of the medium and hence can furnish information on the liquid and liquid mixtures [2]. Studies on speed of sound, viscosity, acoustic thermodynamic, excess thermodynamic parameters and their deviations in the binary systems have been the subject of many investigations in the recent years. These investigations on different systems reveal specific interactions between the molecules of the component liquids, it has been reported by several workers [3]. Theoretical evaluation of speed of sound in binary liquid mixtures and its correlation to study the molecular interactions has been successfully done in recent years [4] using different theoretical relations. The deviations in the values of velocities and adiabatic compressibilities of liquid mixtures with composition are useful to describe the difference in molecular size and strength of interaction between the molecules [5]-[6].

The present work is focused on the study of acoustic, viscometric properties, by measuring the ultrasonic velocities, densities and viscosities of the mixtures of Magnesium salicylate tetrahydrate + 50% ethanol as a solvent. The data obtained can be used to understand intermolecular interactions between the unlike molecules and to test the theories of solutions. By knowing the interaction between the drug molecules and solvent molecules, this work may be helpful to understand the action of drug and this may be useful to create new drugs.

II. EXPERIMENTAL SECTION

A. Materials

Magnesium salicylate tetrahydrate used in the present work was of analytical reagent (AR) grade. The solution was prepared by using 50% mixture of distilled water and 99.99% pure ethanol as a solvent. Weights have been taken on digital electronic balance. (Model-CB/CA/AT-Series).

B. Methods

The ultrasonic velocities have been measured by using ultrasonic Interferometer(Model-M-83). Mittal Enterprises, New Delhi) operating at 4MHz frequency with an accuracy of $\pm 2\text{m/s}$. The viscosities (η) of solution and solvent were determined using Ostwald's viscometer by calibrating with distilled water. The densities (ρ) of the solution were measured accurately using digital densitometer (Model - DMA-35, Anton Paar). The ultrasonic velocity was measured at 4MHz frequency at 298.15K, 303.15K. and 308.15K. The temperature of cell was maintained with continuous circulation of water at constant temperature by using thermostat.

III. RESULTS AND DISCUSSION

The acoustical parameters were calculated from v , η and ρ_s values using standard formulae.

1) Adiabatic Compressibility $\beta = 1/v^2 \rho_s \dots(1)$

2) Free Length $L_f = K \sqrt{\beta_s} \dots(2)$

3) Specific acoustic impedance $Z = V_s \cdot \rho_s \dots(3)$

4) Rao's Constant $R = (M_{\text{eff}}/\rho_s) \times V^{1/3} \dots(4)$

5) Wada's Constant $W = (M_{\text{eff}}/\rho_s) \times \beta^{-1/7} \dots(5)$

6) Apparent Molar Compressibility - $\Phi_K = [1000 (\beta_s \rho_0 - \beta_0 \rho_s) / m \rho_s \rho_0] + (\beta_s M / \rho_s) \dots(6)$

7) Relative Association - $R_A = \rho_s / \rho_0 [V_0 / V_s]^{1/3} \dots(7)$

8) Relaxation time - $\tau = 4/3 \beta \times \eta \dots(8)$

9) Free Volume- $V_f = M_{\text{eff}} \times v_s / k \times \eta \dots(9)$

Where $k = 4.28 \times 10^9$, Temperature Independent Constant for all liquids.

The symbols have their usual meaning.

The experimental data relating to viscosity, density and ultrasonic velocity at 298.15K, 303.15K and 308.15K for frequency 4MHz for the mixture are given in Table no. 1.

Table I: Density, Velocity and Viscosity of Magnesium Salicylate Tetrahydrate in 50% Ethanol as a Solvent at 298.15K, 303.15K, 308.15 K. (Frequency - 4MHz)

Sr.No.	Temperature (°K.)	Concentration (M)	Density(ρ_s) (Kg/m ³)	Velocity(v_s) (m/s)	Viscosity(η) (Pa.S.)or Kg m ⁻¹ s ⁻¹
1	298.15	0.1	944.7	4258.956	4.97E-04
2		0.01	928.6	4578.5498	4.40E-04
3		0.001	930.1	5590.7968	4.57E-04
4	303.15	0.1	942.2	3837.991	4.26E-04
5		0.01	925.9	4846.2534	3.80E-04
6		0.001	927.8	6831.86	3.80E-04
7	308.15	0.1	939.4	4007.1555	3.83E-04
8		0.01	922.8	5097.4751	3.38E-04
9		0.001	924.9	7244.5646	3.39E-04

Table II : Adiabatic Compressibility, Acoustic Impedance and Free length of Magnesium Salicylate Tetrahydrate in 50% Ethanol as a Solvent at 298.15K, 303.15K, 308.15 K. (Frequency - 4MHz)

Sr.No.	Temperature (°K.)	Concentration (M)	Adiabatic Compressibility (β_s) Pa ⁻¹	Acoustic Impedance Z (Kg m ⁻² S ⁻¹)	Free length L_f (m)
1	298.15	0.1	5.836E-11	4.02E+03	1.50E-11
2		0.01	5.137E-11	4.25E+03	1.41E-11
3		0.001	3.4397E-11	5.20E+03	1.15E-11
4	303.15	0.1	7.205E-11	3.62E+03	1.68E-11
5		0.01	4.599E-11	4.49E+03	1.34E-11
6		0.001	2.309E-11	6.34E+03	9.51E-12
7	308.15	0.1	6.629E-11	3.76E+03	1.63E-11
8		0.01	4.17E-11	4.70E+03	1.29E-11
9		0.001	2.06E-11	6.70E+03	9.08E-12

Table III : Relative Association, Apparent Molar Compressibility and Relaxation Time of Magnesium Salicylate Tetrahydrate in 50% Ethanol as a Solvent at 298.15K, 303.15K, 308.15 K. (Frequency - 4MHz)

Sr. No.	Temperature (°K.)	Concentration (M)	Relative Association (R_A)	Relaxation Time (τ)	Apparent Molar Compressibility (ϕ_k)
1	298.15	0.1	1.01E+00	3.86E-14	-1.99E-11
2		0.01	9.69E-01	3.02E-14	-1.05E-09
3		0.001	9.08E-01	2.10E-14	-2.91E-08
4	303.15	0.1	1.03E+00	4.09E-14	6.623E-11
5		0.01	9.38E-01	2.33E-14	-2.28E-09
6		0.001	8.38E-01	1.17E-14	-4.78E-08
7	308.15	0.1	1.00E+00	3.38E-14	-7.29E-11
8		0.01	9.09E-01	1.88E-14	-3.51E-09
9		0.001	8.11E-01	9.31E-15	-5.82E-08

Table IV : Rao's Constant, Wada's Constant, Free Volume of Magnesium Salicylate Tetrahydrate in 50% Ethanol as a Solvent at 298.15K, 303.15K, 308.15 K. (Frequency - 4MHz)

Sr.No.	Temperature (°K.)	Concentration (M)	Rao's Constant (R)	Wada's Constant (W)	Free Volume (V_f)
1	298.15	0.1	1.63E-03	2.91E-03	2.621E-06
2		0.01	1.67E-03	2.96E-03	3.407E-06
3		0.001	1.77E-03	3.12E-03	4.335E-06
4	303.15	0.1	1.57E-03	2.82E-03	2.81E-06
5		0.01	1.70E-03	3.01E-03	4.607E-06
6		0.001	1.90E-03	3.30E-03	7.667E-06
7	308.15	0.1	1.59E-03	2.85E-03	3.494E-06
8		0.01	1.72E-03	3.04E-03	5.866E-06
9		0.001	1.93E-03	3.35E-03	9.877E-06

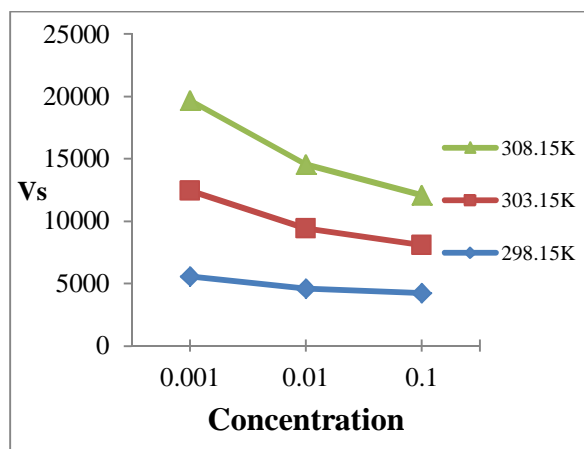


Fig.1 Ultrasonic velocity vs concentration

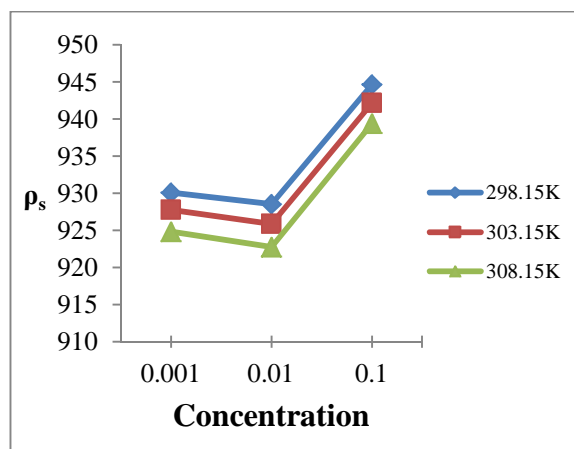


Fig.2 - Density vs Concentration

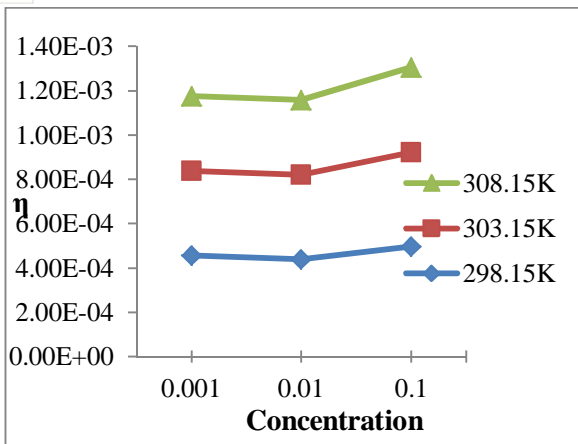


Fig.3 Viscosity vs Concentration

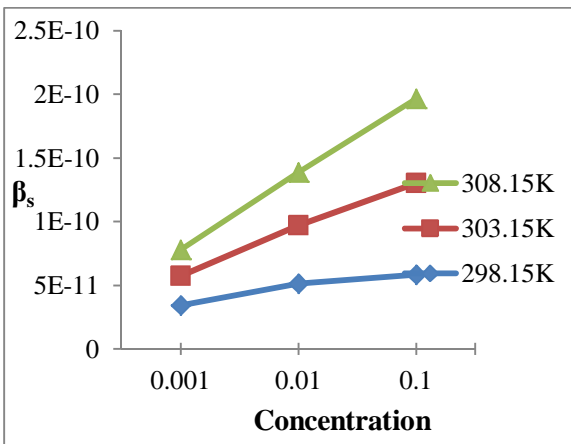


Fig.4, Adiabatic Compressibility (β_s) Vs Conc.

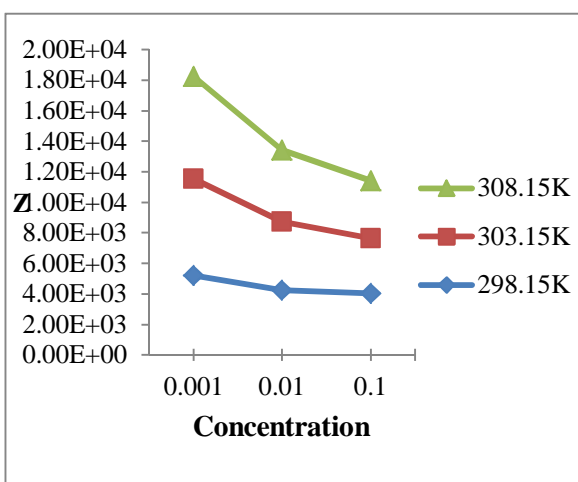


Fig. 5 - Acoustic Impedance (Z) Vs Conc.

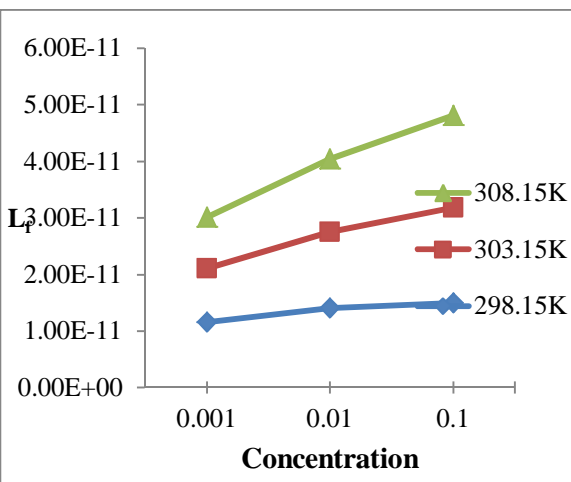


Fig.6 - Free Length (L_f) Vs Conc.

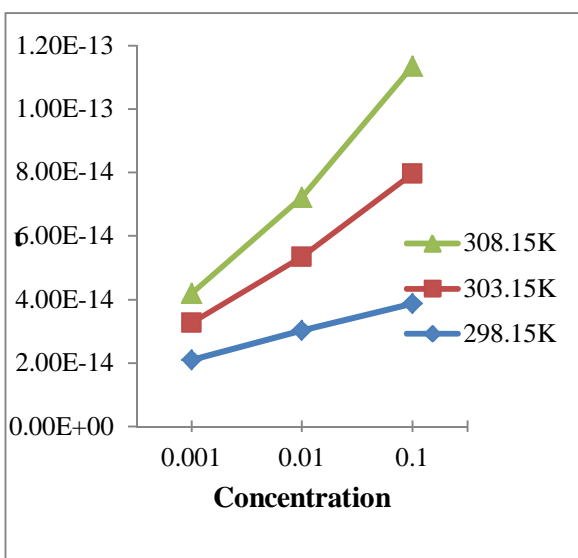


Fig.7 - Relaxation Time (t) Vs Conc.

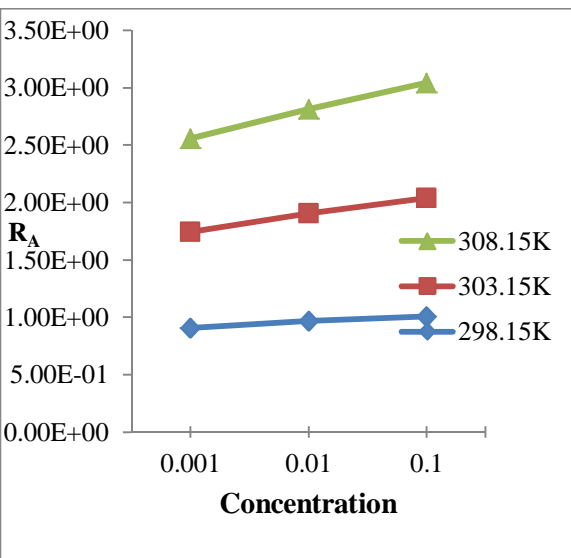


Fig.8 - Relative Association (R_A) Vs Conc

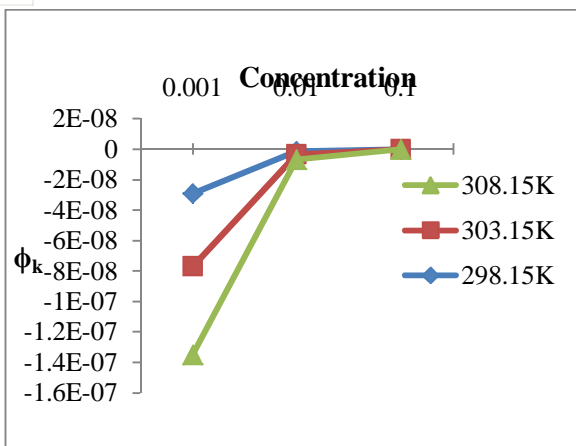


Fig.9 - Apparent Molar Compressibility (ϕ_{κ}) Vs Concentration

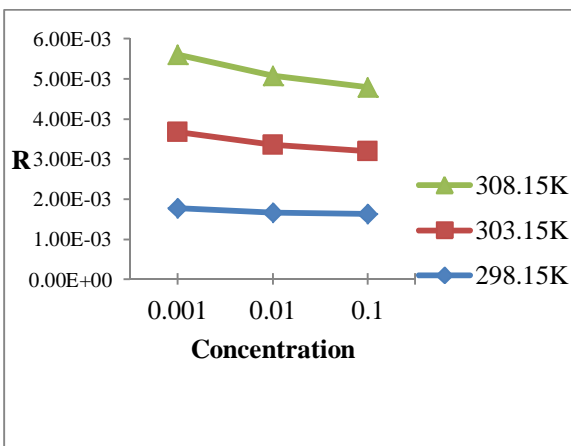


Fig. 10 : Rao's Constant (R) Vs Concentration

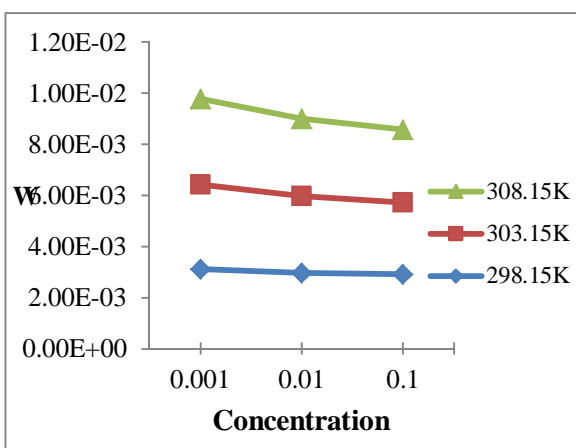


Fig. 11 : Wada's Constant (W) Vs Concentration

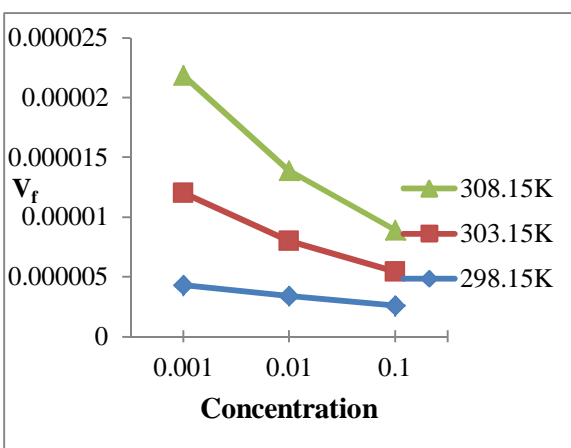


Fig. 12 Free Volume (V_f) Vs Concentration

The variations in the values of ultrasonic velocity and density (ρ_s), Viscosity(η), and different derived parameters at 298.15K, 303.15K and 308.15K and at 4MHz Frequency for sodium salicylate solution in 50% alcohol as solvent are given in the above table 1,2,3 and 4. The ultrasonic velocity has close relation with concentration and temperature. It is observed from the Table- 1 and Fig. 1 that the values of ultrasonic velocity decrease linearly with increase in concentration for temperatures 298.15K, 303.15K and 308.15K. The increase of magnesium salicylate tetrahydrate concentration in the solution decreases the ultrasonic velocity [7]. It may be due to the fact that dense molecules of magnesium salicylate tetrahydrate form strong hydrogen bonds with solvent molecules H_2O and C_2H_5OH . It affects the propagation of ultrasonic waves through the solution. Therefore there may be dipole-dipole interactions. It is observed that, for liquid mixture of magnesium salicylate tetrahydrate in 50% ethanol, the variations in the density and viscosity are not linear with change in concentration. The trend is somewhat different for the liquid mixture with concentration. There are maxima and minima in the values with concentration. Several instances of viscosity variations are reported in literature [8]. The viscosity of the system decreases with increase in the concentration and afterwards viscosity increases with increase in concentration of magnesium salicylate tetrahydrate. It is well known that ethanol and water molecules are highly polar and in addition, they can accept as well as donate protons. Hence the dipole-dipole and acceptor-proton type interactions are also possible in addition to the already explained hydrogen bonding interactions.

In system magnesium salicylate tetrahydrate + 50% ethanol, the increase in the adiabatic compressibility (Fig. 4) shows significant molecular interactions and the solute molecules are loosely held with solvent molecule (water and Ethanol) in the system. The hydrogen bond formation weakens the intermolecular forces resulting in the increase of adiabatic compressibility which indicates that the molecules are not closely packed [9].

The decrease in acoustic impedance with increase in concentration (Fig. 5) of the solution can be explained on the basis of molecular interactions between solutes and solvent molecules which decreases the intermolecular distance making relatively shorter gap between the molecules and become responsible for the propagation of ultrasonic waves.

From fig. 6, it is observed that the intermolecular free length increases with increase in concentration of solute in the liquid system. It shows that there are weaker molecular interactions [10]. The values of relaxation time for system are found to increase with increase in concentration (Fig. 7). These values are in the order of 10^{-14} seconds due to the structural relaxation process showing the presence of molecular interactions. Variation in the values of relative association shows that salvation process is predominant over the breaking of solvent molecules and results in the dipole-dipole interactions because both the solvent molecules (water and ethanol) are polar in nature. The higher molar compressibility of magnesium salicylate tetrahydrate at lower concentration may be due to breakdown of associated alcohol cluster in the bulk phase creating concentrated less efficient packing and hence relatively higher compressibility. The linear decrease in W with concentration shows the weaker molecular interactions due to competition between water and ethanol in the process of salvation of solute.

The variation in the values of free volume is graphically shown in fig. 12 respectively. Here it is found that free volume decreases with increase in concentration [11]-[12] of the solution in both the solvents. It indicates that the space between the solute molecules and solvent molecules decreases. It means they are closely packed.

IV. CONCLUSION

Linear variation in ultrasonic velocity and adiabatic compressibility, acoustic impedance, free length, relaxation time relative association apparent molar compressibility, free volume, Rao's constant and Wada's constant is observed in solvent 50% ethanol, It shows that significant molecular interactions are observed in solvent 50% ethanol. As both the functional groups $-\text{COOH}$ and $-\text{OH}$ of salicylic acid molecule are blocked by Mg^{2+} in magnesium salicylate tetrahydrate, the salvation process is significant and more effective in 50% ethanol. Negative values of apparent molar compressibility are due to solute-solvent molecular interactions. Due to highly polar nature of water and ethanol, the dipole-dipole and acceptor-proton type interactions are also possible in addition to the hydrogen bonding interactions.

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