Ultrasonic analysis of ternary liquid mixture of riboflavin with water and methanol at 288K

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Abstract. In the present study, density, viscosity and ultrasonic velocity have been measured for ternary liquid system of Riboflavin with water and methanol at 288 K in the concentration range 0.00 to 0.1 M. These measured values and derived parameters were used to performed molecular interaction study at 2 MHz using ultrasonic interferometer technique. The results of reported study have been thoroughly analysed and eventually interpreted at the possible molecular interaction such as structure making, solute-solvent and hydrogen bonding effect in the liquid solution of Riboflavin with water and methanol.

Key words: ultrasonic velocity, ternary liquid system, interaction, hydrogen bonding

1. Introduction

Ultrasonic is one of the most useful technique to check the physical and chemical properties of the solution [1-8]. This technique has gained much more insight about the nature of liquid. It explicated most of the properties of liquids and solutions like nature of molecular interaction, inter and intra molecular association and complex formation etc. [9]. The literature study reveals that most of the study of pure liquid as well as binary and ternary liquid mixtures were carried out by many researchers [10-17].

In the recent year, molecular interaction study of water soluble vitamins with methanol has acquired a great importance in pharmaceutical and food industries to prepare various drug dosages, solutions, tablets and capsules etc. [18]. Riboflavin is one of the water soluble vitamin also known as Vitamin- B₂ generally occur in food sources such as eggs, fish, meat, mushroom and milk [19]. It supports the energy metabolism and normal vision of the human body. Methanol used as a solvent in the present study usually found in our dietary sources such as fresh fruits, juices and vegetables [20]. The liquid mixture of Riboflavin and methanol are generally found in our human body and therefore mixture of these two components along with water were taken into the consideration for this investigation. In literature, it has been found that no such data were available for ultrasonic analysis of Riboflavin with water and methanol at 288K, therefore, the present investigation has been carried out using the ultrasonic interferometer technique at 2MHz.

In this communication, we have reported the ultrasonic velocity, density, viscosity and derived thermodynamic parameters for the ternary liquid system of Riboflavin + water + methanol. These
parameters were discussed in terms of solute-solvent interaction through intermolecular hydrogen bonding at 288K.

2. Materials and methods
Riboflavin (Molecular weight 376.36 g/mole) used in the present work was the product of Analytical Reagent (AR) grades with a minimum assay of 99.9%. The various concentrations of solution (0.00 M to 0.1 M) were prepared immediately before use. All the prepared concentrations were stored in airtight bottle to avoid evaporation. The ultrasonic interferometer of 2 MHz frequency was used to measure the ultrasonic velocities of liquid mixture with an accuracy of ± 0.1 ms⁻¹. The Ostwald’s Viscometer was used to measure viscosity of the solution. The time taken for the given volume of liquid between the Viscometer marks was measured using digital stopped clock with an accuracy of ±0.01 Sec. The density measurements of the ternary liquid solution were made accurately using 25 ml specific gravity bottle. Digital balance having an accuracy of 0.1mg was used for weighing purposes. Digitally operated thermostat was used to maintain uniform temperature of the solution throughout the experiment. The accuracy of temperature measurements was ±0.1 K.

2.1. Theoretical aspects
The following parameters were used to find out the molecular interaction study of ternary liquid mixture of the system.

2.1.1. Ultrasonic Velocity: The ultrasonic velocity of liquid can be measured by using the following formula.

\[ U = \frac{2d}{T} \]

\[ = 2d \times v \] (\( \frac{1}{T} = v \))

\[ = \lambda \times v \] \((2d = \lambda) \) \((m/Sec)\)

Where, \( v \) - Frequency of ultrasonic interferometer.
\( d \) – Separation between transducer and reflector.
\( T \) – Travel time period of ultrasonic wave.

2.1.2. Density: The density of the liquid mixture can be given by

\[ \rho = \left( \frac{W}{W_w} \right) \rho_w \] \((Kg/m^3)\)

Where, \( \rho \) - Density of experimental liquid
\( W \) - Weight of liquid or liquid mixture at desired temperature.
\( W_w \) - Weight of water at desired temperature.
\( \rho_w \) - Density of water at desired temperature.

2.1.3. Viscosity: The viscosity of the liquid mixture can be given by

\[ \eta = \left( \frac{\rho \times t_1}{\rho_w \times t_w} \right) \eta_w \] \((Pa.Sec)\)

Where, \( \eta \) - Viscosity of experimental liquid.
t₁ - Flow time of liquid mixture at desired temperature.

t₂ - Flow time of water at desired temperature.

ηw - Viscosity of water at desired temperature.

2.1.4. Adiabatic Compressibility: The adiabatic compressibility values of the solution were calculated as [21],

\[ \beta_a = \frac{1}{U^2 \rho} \quad (\text{Kg}^{-1}.\text{m}.\text{sec}^2) \]  

(4)

Where, U - Ultrasonic Velocity of solution at desired temperature.

\[ \rho - \text{Density of solution at desired temperature.} \]

2.1.5. Free Length: Jacobson [22] in 1951 established a semi-empirical relation to achieve the concept of free length in order to explain the ultrasonic velocity in liquids.

\[ L = K^{1/2} \beta_a \]  

(5)

Where, K - Temperature depended constant.

\[ = 2.131 \times 10^{-6} \]

\[ \beta_a - \text{Adiabatic compressibility.} \]

2.1.6. Acoustic impedance: The acoustic impedance of the liquid can be calculated by using ultrasonic velocity and density as

\[ Z = U. \rho \quad (\text{Kg}/\text{m}^2.\text{sec}) \]  

(6)

2.1.7. Relaxation time: Relaxation time is the time at which molecules return to their original position after being displaced by the force. The relaxation time is estimated from the following relation [23].

\[ \tau = \frac{4}{3} \eta \beta_a \]  

(7)

2.1.8. Free Volume: The dimensional relation given by Suryanarayana and Kuppusamy [24] which is based on ultrasonic velocity (U) and Viscosity (η) data as given below.

\[ V_f = \left( \frac{MU}{K \eta} \right)^{3/2} \quad (\text{m}^3/\text{mole}) \]  

(8)

Where, U - Ultrasonic Velocity of solution at desired temperature.

\[ \eta - \text{Viscosity of solution at desired temperature.} \]

K - Temperature Independent Constant

\[ = 4.28 \times 10^9 \]

M=Σ(mi,xi), Resultant molecular weight of mixture.

(Where: mi and xi are the molecular weight and mole fraction of individual constituents respectively)

2.1.9. Internal pressure: In 1979, Suryanarayana [25] established a relationship to obtain internal pressure using the concept of free volume as

\[ \pi_{in} = bRT \left( \frac{K_{in}}{U} \right)^{1/2} \left( \rho^{2/3} \right) \left( \frac{M^{1/6}}{\eta} \right) \]  

(N/m²)  

(9)
Where, b - Cubic Packing factor.
R - Universal gas constant
T - Absolute temperature (in Kelvin)
K₁ - Temperature independent constant
= 4.28 x 10⁹
M- Resultant molecular weight of mixture.

3. Results and Discussions
The observed experimental values of ultrasonic velocity (U), density (ρ) and viscosity (η) of pure solvent methanol are used in the reported work and matched with the available literature data at 288 K. These values are reported in table 1 and a satisfactory agreement was found.

The various acoustical parameters like adiabatic compressibility (βₐ), acoustical impedance (Z), relaxation time (τ), free length (Lₕ), free volume (Vₕ) and internal pressure (πₕ) were determined from experimental observed values of density (ρ), viscosity (η) and ultrasonic velocity (U) at 288 K by using standard equations 4 to 9 (As mentioned in theoretical part). These parameters were tabulated in table 2 and related graphs were shown in figure 1 to 8.

In the present investigation, it has been observed that, ultrasonic velocity increases with increase in molar concentrations of Riboflavin as shown in figure 1. This may be due to increase in intermolecular hydrogen bonding between Riboflavin (Vit-B₂), water and methanol molecules [28]. The Hydrogen (H⁺) of water or methanol and Oxygen (O⁻) of Riboflavin form a Hydrogen bond, thus association may be possible between Riboflavin, water and methanol molecules through hydrogen bonding. The increase in ultrasonic velocity forms the closed-packed structure and hence the solution becomes stiff for the propagation of ultrasonic wave [29-31]. This suggests a structure promoting behaviour of Riboflavin [32].

In figure 2, density (ρ) seems to be relatively enhanced by an increase in molar concentrations signifies the associative nature and the structure making effect of Riboflavin [32]. It also indicates the hydrophilic nature of Riboflavin in water and methanol.

Figure 1. Variation of ultrasonic velocity with molar conc.  Figure 2. Variation of density with molar conc.
Table 1. Comparison between measured and literature value of density (ρ), viscosity (η) and ultrasonic velocity (U) of pure methanol at 288 K.

| Organic liquid (Solvent) | ρ (Kg.m⁻³) | η (Pa.sec) | U (m/Sec²) |
|--------------------------|------------|------------|------------|
| Present work             | Literature work [26] | Present work | Literature work [27] | Present work | Literature work [26] |
| Methanol                 | 796.4      | 790        | 0.000637   | 0.000635    | 1148        | 1175                  |

Table 2. The measured parameters, Ultrasonic velocity(U), density (ρ), viscosity (η) and derived acoustical parameters i.e adiabatic compressibility (βa), acoustical impedance (Z), relaxation time (τ), free length (Lf), free volume (Vf) and internal pressure (πin) for Riboflavin + methanol in aqueous solution at 288K.

| Conc. (Mole/dm³) | U (m.s⁻¹) | ρ (Kg.m⁻³) | η (Pa.Sec) | Z X 10⁶ (Kg.m²/Sec³) | τ X 10⁻¹⁴ (Sec) | μa X 10⁻¹⁰ (N⁻¹.m²) | Lf X 10⁻¹ (m) | Vf X 10⁻₈ (m³/mole) | πin X 10⁹ N/m² | τ X 10⁻¹³ (Sec) |
|-----------------|-----------|------------|------------|----------------------|----------------|----------------------|----------------|----------------------|----------------|----------------|
| 0               | 1148      | 796.4      | 0.000637   | 0.914                | 8.092          | 0.596                | 4.955          | 1.11                 | 8.092          |
| 0.02            | 1308      | 836.9      | 0.001072   | 1.09                | 9.083          | 6.98                 | 5.107          | 2.817                | 1.37           | 9.083          |
| 0.04            | 1488      | 899.7      | 0.00136    | 1.34                | 9.103          | 5.02                 | 4.330          | 2.440                | 1.50           | 9.103          |
| 0.06            | 1572      | 953.5      | 0.001519   | 1.50                | 8.595          | 4.24                 | 3.981          | 2.289                | 1.58           | 8.595          |
| 0.08            | 1564      | 990.2      | 0.001302   | 1.55                | 7.167          | 4.13                 | 3.926          | 2.919                | 1.48           | 7.167          |
| 0.1             | 1464      | 1010.2     | 0.001048   | 1.48                | 6.454          | 4.62                 | 4.153          | 7.365                | 0.806          | 6.454          |

Acoustic impedance (Z) is a very convenient property of the solution. It explained how much amount of resistance encounters as it passes through the solution. The acoustic impedance increases with increase in Riboflavin concentrations as shown in figure 3. This suggests enhancement in the molecular packing of the medium, which support the possibility of molecular interaction may be due to the formation of hydrogen bonding between aqueous Riboflavin and methanol molecules [33-35].

Relaxation time is a cumulative effect of ultrasonic velocity, density and viscosity [36-37]. The relaxation time occurs due to the structural relaxation process and it is presumed that the molecules get rearranged as a result of the cooperative process [38]. In figure 4, Relaxation time shows an increasing trend up to 0.02 molar concentration. This indicates that a solution of aqueous Riboflavin and methanol, absorbing more amount of ultrasonic energy and therefore the solution is much ordered may be due to hydration [39]. The relaxation time decreases from 0.02 molar concentration may be due to breakage of intermolecular interaction [40]. The observed trend of relaxation time with molar concentrations attributed to the structural changes due to the existence of significant molecular interaction between aqueous Riboflavin and methanol molecules.
Adiabatic compressibility that changes with the structure [41]. The values of adiabatic compressibility decreases with increase in molar concentrations of Riboflavin as shown in figure 5, indicates a close packing of molecules resulting structure making effect of aqueous Riboflavin by methanol molecules [42].

Free length ($L_f$) is one of the crucial acoustic property to determine the distance between the surface of the neighbouring molecules [43]. It also gives the idea of intermolecular interactions between the solute and solvent molecules. This interaction has considerably changed the structural arrangement of neighbouring molecules [44]. The behaviour of free length is analogous to adiabatic compressibility but inversely reflected by ultrasonic velocity [28]. In the present investigation free length shows a decreasing trend with an increase in molar concentrations of solute as indicated in figure 6, confirm the presence of strong interaction among aqueous Riboflavin and methanol molecules. This indicates the structure promoting behaviour of Riboflavin [45].

As observed in figure 7 and 8, free volume decreases and internal pressure increases up to 0.06 molar concentration. This may be due to the existence of strong interaction between the component molecules. However, after 0.06 molar concentration free volume increases, whereas internal pressure decreases with further increase in molar concentrations. This may occur because after 0.06 molar concentration, the molecules get disordered due to increases entropy of the system which may leads to decrease interactions between the aqueous Riboflavin and methanol molecules.
Figure 7. Variation of free volume with molar conc. Figure 8. Variation of internal pressure with molar conc.

4. Conclusions
The results obtained from the present study reveals the existence of solute-solvent interaction. This promotes the structure making tendency of Riboflavin due to the formation of hydrogen bonding between aqueous Riboflavin and methanol molecules.

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