Acoustic and viscometric studies of ternary liquid mixtures of aqueous sodium methyl p-hydroxybenzoate with polyethylene glycols at 25°C

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Abstract

The various ultrasonic parameters like acoustic impedance, adiabatic compressibility, intermolecular free length, relaxation time, relative association, attenuation and Gibb’s free energy of polyethylene glycols with molecular weight 200 and 600 in aqueous sodium methyl para-hydroxybenzoate is evaluated at 25°C from the density, speed of sound and viscosity. Jone-Dole’s equation has been employed to analyze the experimental results of viscosity. The existence of interaction among the fragments of ternary liquid mixtures has been determined from viscosity coefficients. The polyethylene glycols act as the structure builder in water. The viscosity coefficient B surges with escalation in molecular mass of polyethylene glycols. The structure builder property of polyethylene glycols follows the order PEG-600 > PEG-200.

Keywords: Density, speed of sound, viscosity, Jone-Dole’s equation

1. Introduction

The inspection of studies regarding volumetric, acoustic and viscometric of solution is of great significance to provide the knowledge concerning various interactions midst the components of the fragments and hence these studies are helpful in various technological and biological procedures [1, 2]. The work on medicinal purpose used substances needs the attention of people in every parts including nature of acoustic. Solvents serve a substantial role in chemicals preparing and application processing. Almost all the chemical reaction or intermediate are usually performed in mixtures. The measurements of liquid viscosity and solution mixtures are often used in latest years to analyze physico-chemical nature. The physical characteristics of the fluid play an important part in the growth of the distinct component formulation and evaluation [3, 4]. The assessment of the transmission and absorption of acoustic waves is one of the significant techniques of investigating material characteristics in 3 states. Acoustic parameters are widely used to research molecular interactions in binary liquid pure compounds [5, 6]. The research of binary liquid mixtures has drawn several scientists in the field due to latest advances in theories of liquid mixtures and experimental techniques [7]. Speed of sound and its derived ultrasonic parameters viz. acoustic impedance, relaxation time, adiabatic compressibility, free length together with their excess data provide useful molecular environment data [8-10]. The thermodynamic and speed of sound variable has been utilized to analyze multiple types of connections, movement of fragments, interaction forms and their abilities [11, 12].

PEG is an ethylene oxide and water condensing polymer. In many organic solvents and water, it is soluble. In polyethylene glycols, both the forms of intra and inter molecular molecular hydrogen bonds are formed to improve water solubility and major organic solvents [13]. Latest research has been
Conducted on PEGs viscosity in water and other solvents. [14-17]. Parabens in cosmetics and pharmaceuticals are a class of frequently utilized preservatives. They are chemically the sequence of parahydroxybenzoates. Parabens are widely taken as preservatives in pharmaceutical and cosmetic products, food and beverages [18]. Multiple researches is carried on thermo-physical characteristics of polyethylene glycols and parabens solutions but nothing is studied on intermolecular association study of ternary mixture of polyethylene glycols 200 with paraben. In the present research the nature of ternary mixtures of polyethylene glycols in sodium methylparaben water solutions has been investigated through density, ultrasonic velocity and viscosity data at 25°C. The various acoustical parameters are derived from the measured data and hence results are interpreted in regard to associations among fragments in the present studied system.

2. Chemicals and Techniques

Chemicals
Polyethylene glycols with the molecular mass 200 and 600 and sodium methylparaben with molecular mass 174.13 of 99% AR grade has been utilized in the present investigation. All the chemicals were received from Loba chemie Pvt. Ltd. India. The data for density and ultrasonic speed was evaluated via Anton Paar DSA 5000 M density and velocity meter on the other hand the viscosity has been measured by Oswald’s viscometer. For studying the impact of temperature, every viscosity measurement was carried out in water thermostat with an accuracy of ±0.001 K. ‘ORIGIN’ software has been employed to plot the graphs.

Methods
Various ultrasonic parameters are derived from the following formula:

**Acoustic impedance**  
\[ Z = \rho \times U \]

**Adiabatic compressibility**  
\[ \beta = \frac{1}{(U^2 \times \rho)} \]

**Intermolecular free length**  
\[ L_f = K_B \times \beta^{1/2} \]

Where, \( K_B \) = Jacobson constant

**Ultrasonic Attenuation**  
\[ \alpha/f^2 = \frac{8\pi^2 \eta}{3pU^3} \]

**Relaxation Time**  
\[ \tau = 4\beta\eta/3 \]

**Relative strength**  
\[ r = 1-[U/U_\infty] \]

**Relative association**  
\[ R_A = (\rho/\rho_0)/(U_0/U)^{1/3} \]

**Gibb’s Free Energy**  
\[ \Delta G = K_B T \ln (KB T \tau/ h) \]

**Viscosity measurement**

The Oswald’s viscometer was employed to find the viscosity of ternary liquid mixtures of PEGs 200 and 600 in aqueous solution of sodium methylparaben at 25°C by evaluating time of flow through capillary of constant volume of mixture. The stop watch was utilized having the accuracy of 0.1 seconds. The viscosity measurement is done with the help of following expression:

\[ \eta_2 = \eta_1 \left( \frac{t_2}{t_1} \right) \left( \frac{\rho_2}{\rho_1} \right) \]

Where, \( \eta_1 \) = viscosity of water, \( \eta_2 \) = viscosity of experimental solution, \( \rho_1 \) = density of water, \( \rho_2 \) = density of experimental solution, \( t_1 \) = time of flow of water, \( t_2 \) = time of flow of experimental solution. To find the interaction parameters in aqueous solutions the data of viscosity at various concentrations has been employed. The Jone-Dole’s equation has been utilized to determine these interaction parameters as:
\[ \frac{(\eta_0 / \eta - 1)}{\sqrt{C}} = A + B \sqrt{C} \]

Where \( C \) is the molar concentration, \( A \) and \( B \) are solute-solute and solute-solvent interaction coefficients.

3. Result and discussion

The viscosity for ternary mixtures of polyethylene glycols in aqueous (0.00 and 0.01) mol.kg\(^{-1}\) sodium methyl para-hydroxybenzoate at different concentrations and at temperature \( T = 25^\circ C \) are measured. The data of density and speed of sound of aqueous PEG-200 and PEG-600 in sodium methyl para-hydroxybenzoate at 25\(^\circ C\) temperature has been taken from our earlier paper [19]. From the measured parameters various ultrasonic parameters are computed and are presented in Table 1 and Table 2.

**Table 1.** Computed values of acoustic impedance (Z), adiabatic compressibility (\( \beta \)), intermolecular free length (\( L_i \)), Gibb's free energy (\( \Delta G \)) and relative association (\( R_A \)) for ternary liquid mixture at 25\(^\circ C\)

| Concentration (m) | PEG-200 | PEG-600 |
|-------------------|---------|---------|
| \( \eta_0 = 0.00 \) |        |         |
| 0.0000            | 1.491   | 1.491   |
| 0.0982            | 1.506   | 1.507   |
| 0.1937            | 1.519   | 1.521   |
| 0.2865            | 1.533   | 1.536   |
| 0.3768            | 1.547   | 1.550   |
| 0.4648            | 1.561   | 1.564   |
| \( \eta_0 = 0.01 \) |        |         |
| 0.0000            | 1.491   | 1.491   |
| 0.0978            | 1.507   | 1.507   |
| 0.1922            | 1.521   | 1.521   |
| 0.2910            | 1.536   | 1.536   |
| 0.3810            | 1.550   | 1.550   |
| 0.4724            | 1.564   | 1.564   |

**Table 1**
Figure 1 represents the deviation of acoustic impedance with different concentration for ternary mixture of polyethylene glycols in aqueous sodium methyl para-hydroxybenzoate at 25°C.
The reflection and transmission of sound waves are affected by this significant factor in solvent molecules as well as in medium [20]. The value of impedance varies linearly with concentration indicating the occurrence of strong interaction between liquid mixtures inspected. The value of impedance increases from PEG-200 to PEG-600 with the concentration indicating that the molecules in PEG-600 are strongly interacted as compared to PEG-200. The value of adiabatic compressibility (Table 1) decreases with rise in the concentration of solute as well as with sodium methyl para-hydroxybenzoate concentration. It signifies that fragments of the studied ternary liquid mixtures are tightly bounded with each other. It indicates that the molecules of PEG-600 are tightly bound with each other as compared to PEG-200. Hence, adiabatic compressibility is behaving oppositely with respect to ultrasonic speed therefore, supporting the formula. The deviation of intermolecular free length w.r.t. concentration is indexed in Table 1. The $L_f$ falls with escalation in concentration of polyethylene glycols and sodium methyl para-hydroxybenzoate. Both the compressibility and free length possess same behaviour as depicted by their mathematical expression which is in agreement with experimental results. The data of Gibb’s free energy with concentration is presented in Table 1. The information regarding transformation of energy in response to chemical reaction is provided by Gibb’s free energy which is utilized to do work. It is found that the data of Gibb’s free energy is inconsistent with the addition of solute. There exists the linear deviation of relative association with concentration. The relative association data increases with concentration escalation. The value increases from PEG-200 to PEG-600. It is examined from the close values of relative association that investigated ternary liquid mixture is essentially ideal in nature.

![Graph of acoustic impedance with concentration at 25°C.](image)

**Figure 1.** Graph of acoustic impedance with concentration at 25°C.
Table 2 Computed values of viscosity, relaxation time, ultrasonic attenuation for ternary liquid mixtures at 25°C.

| (m) PEG | Concentration | Viscosity ($\eta$) | Relaxation Time ($\tau$) s x 10^{-5} | Ultrasonic Attenuation ($\alpha/\xi^2$) s^{-2} m^{-1} x 10^{-12} |
|---------|---------------|-------------------|--------------------------------------|-----------------------------------------------|
| (0.00)  | 0.0000        | 0.8942            | 5.3442                               | 7.045                                         |
|         | 0.0982        | 0.8987            | 5.2819                               | 6.914                                         |
| PEG-200 | 0.1937        | 0.9128            | 5.2842                               | 6.874                                         |
|         | 0.2865        | 0.9191            | 5.2394                               | 6.773                                         |
|         | 0.3768        | 0.9324            | 5.2340                               | 6.723                                         |
|         | 0.4648        | 0.9405            | 5.1982                               | 6.634                                         |
| (0.01)  | 0.0000        | 0.8959            | 5.3414                               | 7.034                                         |
| PEG-200 | 0.0978        | 0.9048            | 5.3109                               | 6.949                                         |
|         | 0.1922        | 0.9469            | 5.4731                               | 7.116                                         |
|         | 0.2910        | 0.9180            | 5.2190                               | 6.739                                         |
|         | 0.3810        | 0.9243            | 5.1751                               | 6.640                                         |
|         | 0.4724        | 0.9482            | 5.2249                               | 6.660                                         |
| (0.00)  | 0.0000        | 0.9110            | 5.4448                               | 7.178                                         |
| PEG-600 | 0.1028        | 0.9247            | 5.2695                               | 6.813                                         |
|         | 0.1957        | 0.9382            | 5.1209                               | 6.507                                         |
|         | 0.2925        | 0.9526            | 4.9721                               | 6.204                                         |
|         | 0.3879        | 0.9716            | 4.8517                               | 5.946                                         |
|         | 0.4853        | 0.9833            | 4.6935                               | 5.648                                         |
| (0.01)  | 0.0000        | 0.9173            | 5.4688                               | 7.202                                         |
| PEG-600 | 0.1002        | 0.9306            | 5.2944                               | 6.841                                         |
|         | 0.1962        | 0.9430            | 5.1294                               | 6.507                                         |
|         | 0.2899        | 0.9592            | 4.9941                               | 6.224                                         |
|         | 0.3876        | 0.9745            | 4.8473                               | 5.930                                         |
|         | 0.4873        | 0.9987            | 4.7415                               | 5.692                                         |

Table 2 indicates the linear deviation of relaxation time with concentration. Relaxation time is dependent on adiabatic compressibility as well as on viscosity and hence, relaxation time behaves similar to viscosity. The strength of intermolecular forces increases with surge in the viscosity leading to rise in relaxation time. The acoustical parameters ultrasonic attenuation and relaxation time are related to each other. Loss of the sound wave is termed as time delay between passing of ultrasonic wave and getting back of molecule to its equilibrium position. Hence, with increase in the molality concentration of polyethylene glycols, ultrasonic attenuation increases. The larger relaxation time and viscosity w.r.t. structural relaxation process is responsible for ultrasonic attenuation escalation with concentration. In studying the structural and molecular properties of molecular components the structural relaxation process plays very vital role.

The data of $\eta_0 / \eta$ with the concentrations for ternary mixture of polyethylene glycols in aqueous sodium methylparaben have been collected. The interaction parameter in the aqueous solutions of polyethylene glycols with sodium methyl para-hydroxbenzoate has been computed from the values of viscosity. Hence, Jone-Dole’s equation has been employed to study the interaction parameter as follows:

$$\frac{(\eta_0 / \eta - 1)}{\sqrt{C}} = A + B\sqrt{C} \quad (1)$$
Where \( C \) is the molar concentration, \( A \) and \( B \) are the coefficients of the solute-solute and solute-solvent interaction. The \( B \) values were attained from the linear plot among \( \sqrt{C} \) and \( (\eta_0/\eta-1)/\sqrt{C} \). The plot between \( \sqrt{C} \) and \( (\eta_0/\eta-1)/\sqrt{C} \) is represented in Figure 2.

![Figure 2](a) PEG-200

![Figure 2](b) PEG-200
Figure 2. Graph of $(\eta_0 / \eta - 1)/\sqrt{C}$ with $\sqrt{C}$ at 25°C.

The A and B coefficients are indexed in Table 3 which are computed from slopes and intercepts of the ternary solution. The data of coefficient B is positive which indicate the existence of sturdy associations midst solute-solvent fragments. The B coefficient surges from PEG 200 to PEG-600. The values of B signify that these polyethylene glycols act as a structure builder.
Table 3 Computed values of $\eta_0/\eta$ and concentration for ternary liquid mixtures at 25$^\circ$C.

| (m) | PEG | concentration | $\sqrt{C}$ | $\eta_0/\eta$ | $(\eta_0/\eta-1)/\sqrt{C}$ |
|-----|-----|---------------|-------------|---------------|-----------------------------|
| (0.00) | PEG-200 | 0.0982 | 0.3135 | 0.0269 | 0.1033 |
|      |      | 0.1937 | 0.4402 | 0.0323 | 0.1104 |
|      |      | 0.2865 | 0.5353 | 0.0376 | 0.1157 |
|      |      | 0.3768 | 0.6139 | 0.0428 | 0.1201 |
|      |      | 0.4648 | 0.6818 | 0.0478 | 0.1239 |
| (0.01) | PEG-200 | 0.0978 | 0.3128 | 0.0433 | 0.1608 |
|      |      | 0.1922 | 0.4385 | 0.0559 | 0.1699 |
|      |      | 0.2910 | 0.5395 | 0.0582 | 0.1772 |
|      |      | 0.3810 | 0.6173 | 0.0624 | 0.1828 |
|      |      | 0.4724 | 0.6874 | 0.0751 | 0.1878 |
| (0.00) | PEG-600 | 0.1028 | 0.3207 | 0.1216 | 0.4062 |
|      |      | 0.1957 | 0.4425 | 0.1223 | 0.4164 |
|      |      | 0.2925 | 0.5408 | 0.1301 | 0.4247 |
|      |      | 0.3879 | 0.6229 | 0.1472 | 0.4316 |
|      |      | 0.4853 | 0.6967 | 0.1505 | 0.4378 |
| (0.01) | PEG-600 | 0.1002 | 0.3165 | 0.3165 | 0.4839 |
|      |      | 0.1962 | 0.4430 | 0.4429 | 0.4953 |
|      |      | 0.2899 | 0.5384 | 0.5383 | 0.5039 |
|      |      | 0.3876 | 0.6226 | 0.6225 | 0.5115 |
|      |      | 0.4873 | 0.6981 | 0.6980 | 0.5183 |

The order of the structure builder solutes follows trend: PEG 600 > PEG 200. The coefficient A is considered to be positive for electrolytes, on the other hand it is considered as zero for non-electrolyte [21]. The eq. (1) can be reduced to eq. (3) as:

$$\frac{\eta_0}{\eta-1} = BC$$  \hspace{1cm} (2)

The data of viscosity $\eta_0/\eta$ of ternary solutions at constant temperature is dependent on molar concentration (C) which is represented by the following Straundinger equation [22-24]:

$$\eta-\eta_0/\eta_0 = knCn$$  \hspace{1cm} (3)

$n$ is the number of monomer, $C$ is the molar concentration and $k$ is the constant for the given solute in solvent. The values of $\eta_0/\eta-1$ and $kn$ are indexed in Table 3 and 4. It has been clear from the eq (2) and (3) that the value of B is equal to $kn$ values. The molecular mass of polyethylene glycols has been employed to compute the number of monomers. The values of $n$ for PEG-200 and PEG-600 have been collected in Table 4. The value of constant $k$ has been calculated from the value of B and n. The data of $B$ attained from the plots has been perceived in Table 4 which posses same magnitude and follows the consistency with the experimental data. The obtained experimental data is consistent with the applicability of equations above. The positive value of B for each polyethylene glycol has the effect of structure builder on the water in the present system studied. The existence of solute-solvent association is indicated by the B values. This association surges with rise in molar mass of polyethylene glycols. The hydrogen bond among water and solute supports the structure builder property. The following equation has been used to compute the hydrodynamics volume as follows:

$$B = 0.0025 V_h$$  \hspace{1cm} (4)

Where $V_h$ represents the hydrodynamics volume. The computed data of $V_h$ has been listed in Table 4.
Table 4: Calculated parameters of stauding and Jon-Dole’s equation for ternary liquid mixture at 25°C

| PEGs   | η₀/η–1 versus C | (η₀/η–1)/√C versus √C | n   | k   | Vₜ×10⁻³ (dm³ mol⁻¹) |
|-------|----------------|------------------------|-----|-----|---------------------|
|       | B/kn (dm³ mol⁻¹) | B/kn (dm³ mol⁻¹)      |     |     |                     |
| (0.00) PEG-200 | 0.056             | 0.056                  | 4   | 0.014 | 0.0224              |
| (0.01) PEG-200 | 0.074             | 0.072                  | 4   | 0.018 | 0.0296              |
| (0.00) PEG-600 | 0.086             | 0.084                  | 13  | 0.086 | 0.0344              |
| (0.01) PEG-600 | 0.097             | 0.090                  | 13  | 0.007 | 0.0388              |

It has been found that the hydrodynamics volume enhances with molecular mass of polyethylene glycols. The variation of $Vₜ$ with low molecular mass is much linear in comparison to the higher molecular mass.

4. Conclusion

The occurrence of associations amid the fragments of mixture is predicted by ultrasonic study of ternary liquid mixtures of polyethylene glycols in aqueous mixtures of sodium methyl parahydroxybenzoates. The ultrasonic speed escalates with increase in the concentration because of decrease in intermolecular free length of the system studied. Every ultrasonic parameter enhances with surge in the concentration. All the acoustical parameters are varying linearly with respect to concentration suggesting the non-existence of complex formation in the system.

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