Molecular interactions in ternary system of ethane-1, 2-diol with methanol and methyl 4-hydroxybenzoate at 298 K: An acoustic approach

Ashima Thakur¹, Harsimran Kaur¹, Nabaparna, K.C. Juglan*¹, Harsh Kumar
¹Department of Physics, Lovely Professional University, Phagwara, 144401, Punjab, India.
²Department of Chemistry, Dr B R Ambedkar NIT, Jalandhar 144011, Punjab, India.
Corresponding author e-mail: kc.juglan@lpu.co.in

Abstract

Density, speed of sound and viscosity of ethane-1,2-diol, methanol and methyl 4-hydroxybenzoate (methylparaben) at different concentrations and at constant temperature T=298K have been measured by Anton Paar DSA 5000 M density and velocity meter and Ostwald’s viscometer respectively. Experimentally measured values of density, speed of sound and viscosity are employed to calculate different ultrasonic parameters like impedance, adiabatic compressibility, intermolecular free length, acoustic attenuation, relaxation time, relative association, relative strength, and Gibb’s free energy. Graphs for each acoustical parameter against concentration are plotted with the help of Origin. The linear variation is found for most of the acoustic parameters which implies the absence of complex formation in ternary system studied.

Keywords: Density; Ultrasonic speed; viscosity; acoustical parameters

1. Introduction

Ultrasonic technique is considered to be very useful device in interpreting the molecular interactions between polar and non-polar components existing in liquid mixture [1]. The inspection of organic liquids through ultrasonic computation stimulates the scientific and practical interest [2-4]. Such kind of study has been establish to provide the information concerning structure of liquid state and intermolecular process [5, 6].The experimental as well as theoretical molecular interaction study of binary liquid mixtures has been widely done [7]; whereas, the study of ternary liquid mixture properties is scarce [8, 9]. The volumetric and viscometric properties of solution mixture provide the affirmation to examine the structural property of liquids [10-15]. The ultrasonic speed computation is used in interpreting the physiochemical behaviour and nature of molecular system in liquid mixture [16-19].

Solutions of glycol in water are extensively used in the manufacture of lubricants, conditioning agents, solvents and hydrosopic agents [20]. Parabens are the family of parahydroxybenzoic acid esters which are widely taken as preservatives in pharmaceuticals, food and beverages, personal care products [21, 22]. From our investigation it is found that numerous works is carried on thermo-physical nature of glycols and parabens solutions but no work is done on intermolecular interaction study of ternary mixture of glycols with paraben. In the present research the nature of ternary mixtures of glycols in methanol solution of methylparaben has been investigated via density, speed of sound.
and viscosity data at 298 K. The different ultrasonic parameters are derived from the measured data and hence results are interpreted in order of molecular associations in the present studied system.

2. Material and Techniques

For the recent investigation ethylene glycol, methanol and methylparaben with molecular mass 62.07 g/mol, 32.04g/mol and 152g/mol of 99% AR grade is utilized. The Anton Paar DSA 5000 M density and sound velocity meter is used to measure the data of density and speed of sound; whereas the viscosity has been measured by Oswald’s viscometer. In order to study the effect of temperature all the viscosity measurements were carried out in water thermostat with an accuracy of ±0.001 K. ‘ORIGIN’ software has been employed to plot the graphs.

Theory of derived parameters

The ultrasonic parameters namely acoustic impedance, adiabatic compressibility, intermolecular free length, relaxation time, ultrasonic attenuation, relative association, relative strength and Gibb’s free energy are derived from the following formula:

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

- **Adiabatic compressibility**
  \[ \beta = 1/ (U^2 \times \rho) \]

- **Intermolecular free length**
  \[ L_f = K_B \times \beta^{1/2} \quad \text{Where, } K_B = \text{Jacobson constant} \]

- **Ultrasonic Attenuation**
  \[ \alpha/f^2 = 8\pi^2\eta/3\rho U^3 \]

- **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**
  \[ \Delta G = K_B T \ln (K_B T \tau/\hbar) \]

3. Result and discussion

The density, ultrasonic speed and viscosity for ternary mixtures of Ethylene glycol + methanol + methylparaben (0.01 and 0.03) mol.kg\(^{-1}\) at various concentrations and at temperature T = 298K are measured. From the measured parameters various ultrasonic parameters are computed and are presented in Table 1 and Table 2.

All the values of density, ultrasonic speed and viscosity for ternary mixture of Ethylene glycol + methanol + methylparaben escalates with increase in concentration. The rise in the acoustic speed with concentration predicts the enhancement of cohesive forces in solvent molecules [23]. The reflection and transmission of sound waves are affected by this significant factor in solvent molecules as well as in medium [24]. The value of acoustic impedance varies linearly with concentration indicating the occurrence of strong interaction between liquid mixtures studied. **Figure 1** displays the deviation of acoustic impedance with concentration for ternary mixture of Ethylene glycol + methanol + methylparaben (0.01 and 0.03) mol.kg\(^{-1}\) at 298K temperature.
| m (mol.kg⁻¹) | concentration | Impedance (Z) kg m⁻² s⁻¹ × 10⁵ | Adiabatic compressibility (β) N/m² × 10⁷ | Intermolecular free length (Lₐ) Å × 10⁻¹⁰ | Relaxation time (τ) s x 10⁻⁵ | Ultrasonic Attenuation (α/f²) s² m⁻¹ × 10⁻¹² |
|--------------|---------------|---------------------------------|------------------------------------------|---------------------------------|--------------------------|------------------------------------------|
| 0.01         | 0.00000       | 873.430                         | 10.340                                   | 6.6138                          | 8.4186                  | 1.501                                    |
|              | 0.09986       | 878.242                         | 10.253                                   | 6.5858                          | 8.6122                  | 1.531                                    |
|              | 0.19552       | 881.555                         | 10.196                                   | 6.5676                          | 8.6998                  | 1.544                                    |
|              | 0.30041       | 885.394                         | 10.130                                   | 6.5463                          | 8.7943                  | 1.557                                    |
|              | 0.39780       | 888.812                         | 10.073                                   | 6.5280                          | 8.8820                  | 1.570                                    |
|              | 0.49906       | 892.278                         | 10.014                                   | 6.5086                          | 8.9602                  | 1.580                                    |
|              | 0.60110       | 895.698                         | 9.960                                    | 6.4910                          | 9.0872                  | 1.600                                    |
|              | 0.71082       | 900.480                         | 9.890                                    | 6.4682                          | 9.1169                  | 1.603                                    |
|              | 0.79912       | 905.180                         | 9.828                                    | 6.4479                          | 9.2301                  | 1.621                                    |
|              | 0.89231       | 909.688                         | 9.768                                    | 6.4284                          | 9.2739                  | 1.627                                    |
| 0.03         | 0.00000       | 875.575                         | 10.296                                   | 0.6243                          | 8.5700                  | 1.525                                    |
|              | 0.10375       | 880.225                         | 10.213                                   | 0.6303                          | 8.5836                  | 1.523                                    |
|              | 0.20032       | 883.555                         | 10.160                                   | 0.6403                          | 8.6744                  | 1.537                                    |
|              | 0.30210       | 887.423                         | 10.094                                   | 0.6500                          | 8.7477                  | 1.547                                    |
|              | 0.39976       | 891.529                         | 10.027                                   | 0.6603                          | 8.8275                  | 1.558                                    |
|              | 0.40190       | 891.391                         | 10.018                                   | 0.6606                          | 8.8242                  | 1.556                                    |
|              | 0.58123       | 898.559                         | 9.921                                    | 0.6769                          | 8.9534                  | 1.575                                    |
|              | 0.69785       | 902.972                         | 9.854                                    | 0.6840                          | 8.9864                  | 1.578                                    |
|              | 0.79901       | 908.114                         | 9.778                                    | 0.6920                          | 9.0212                  | 1.581                                    |
|              | 0.89912       | 914.765                         | 9.689                                    | 0.6980                          | 9.0168                  | 1.578                                    |
| m (mol.kg\(^{-1}\)) | concentration | Gibb's free energy (\(\Delta G\)) KJ mol\(^{-1}\) \(\times 10^{20}\) | relative association (\(R_A\)) | relaxation strength (\(r\)) |
|-------------------|----------------|--------------------------------|-----------------|-----------------|
| 0.01              | 0.0000         | 1.0048                         | 1.0009          | 0.3080          |
|                   | 0.09986        | 1.0056                         | 1.0024          | 0.3059          |
|                   | 0.19552        | 1.0059                         | 1.0038          | 0.3047          |
|                   | 0.30041        | 1.0063                         | 1.0053          | 0.3032          |
|                   | 0.39780        | 1.0066                         | 1.0068          | 0.3019          |
|                   | 0.49906        | 1.0069                         | 1.0080          | 0.3005          |
|                   | 0.60110        | 1.0074                         | 1.0097          | 0.2994          |
|                   | 0.71082        | 1.0075                         | 1.0128          | 0.2982          |
|                   | 0.79912        | 1.0080                         | 1.0166          | 0.2974          |
|                   | 0.89231        | 1.0081                         | 1.0202          | 0.2967          |
| 0.03              | 0.0000         | 1.0054                         | 1.0000          | 0.3067          |
|                   | 0.10375        | 1.0055                         | 1.0016          | 0.3048          |
|                   | 0.20032        | 1.0058                         | 1.0035          | 0.3038          |
|                   | 0.30210        | 1.0061                         | 1.0050          | 0.3023          |
|                   | 0.39976        | 1.0064                         | 1.0069          | 0.3008          |
|                   | 0.40190        | 1.0064                         | 1.0054          | 0.3001          |
|                   | 0.58123        | 1.0069                         | 1.0111          | 0.2989          |
|                   | 0.69785        | 1.0070                         | 1.0135          | 0.2976          |
|                   | 0.79901        | 1.0072                         | 1.0164          | 0.2961          |
|                   | 0.89912        | 1.0072                         | 1.0215          | 0.2949          |
Figure 1. Graph of acoustic impedance against concentration in ethylene glycol+ methanol+ methylparaben at 298K.

Figure 2. Graph of adiabatic compressibility against concentration in ethylene glycol+ methanol+ methylparaben at 298K.

From Figure 2 it is shown that the values of adiabatic compressibility falls with rise in the solute concentration along with the methylparaben concentration. It signifies that molecules of Ethylene glycol + methanol+ methylparaben are tightly bounded with each other. Hence, adiabatic
compressibility is behaving oppositely with respect to ultrasonic speed therefore, supporting the formula. The deviation of intermolecular free length with concentration is displayed in Figure 3. The intermolecular free length falls with escalation in Ethylene glycol and methylparaben concentration. Both adiabatic compressibility and intermolecular free length possess same behaviour as depicted by their mathematical expression which is in agreement with experimental results.

![Graph of intermolecular free length against concentration in ethylene glycol+ methanol+ methylparaben at 298K.](image1)

**Figure 3.** Graph of intermolecular free length against concentration in ethylene glycol+ methanol+ methylparaben at 298K.

![Graph of relaxation time against concentration in ethylene glycol+ methanol+ methylparaben at 298K.](image2)

**Figure 4.** Graph of relaxation time against concentration in ethylene glycol+ methanol+ methylparaben at 298K.

Figure 4 displays 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 leads to relaxation time escalation. 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, Figure 5 shows that with increase in the concentration ultrasonic attenuation increases. The larger data of relaxation time and viscosity with respect to 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.

![Graph of ultrasonic attenuation against concentration in ethylene glycol+ methanol+methylparaben at 298K.](image)

**Figure 5.** Graph of ultrasonic attenuation against concentration in ethylene glycol+ methanol+methylparaben at 298K.

![Graph of relative strength against concentration in ethylene glycol+ methanol+methylparaben at 298K.](image)

**Figure 6.** Graph of relative strength against concentration in ethylene glycol+ methanol+methylparaben at 298K.

From Figure 6 the variation of relative strength with concentration can be seen. The value of relative strength varies inversely with concentration. Figure 7 shows the linear variation of relative association with concentration. The relative association data increases with rise in the concentration. It is
examined from the close values of relative association that investigated ternary liquid mixture is essentially ideal in nature.

Figure 7. Graph of relative association against concentration in ethylene glycol+ methanol+ methylparaben at 298K.

Figure 8. Graph of Gibb’s free energy against concentration in ethylene glycol+ methanol+ methylparaben at 298K.
The plot of Gibb’s free energy w.r.t. concentration is displayed in Figure 8. The Gibb’s free energy provides the information about transformation of energy concerned with the response to chemical which is used in doing work. It can be found from the data that the Gibb’s free energy escalates w.r.t. concentration rise of solute indicate increase in energy change.

4. Conclusion

The occurrence of associations midst the fragments of mixture is predicted by ultrasonic study of ternary solutions of ethylene glycol, methanol and methylparaben. The density, acoustic speed and viscosity increases with rise in the concentration. The ultrasonic speed escalates with increase in the concentration due to fall in intermolecular free length of the solution studied. All the evaluated ultrasonic parameters rises along 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.

References

[1] Elangovan S and Mullainathan S 2012 *Indian J. Phys* 86 727-30
[2] Kannapan V and Santhi R J 2006 *Indian J Pure & Appl. Phys* 44 815-19.
[3] Ali A, Nain A K and Lal B 2005 *Indian J Chem* 44A 511
[4] Seetharaman V, Kalyanasundaram S and Gopalan A 2004 *Indian J Pure & Appl. Phys* 42 735.
[5] Sumathi T and Maheshwari J U 2009 *Indian J Pure & Appl. Phys* 47 782-6
[6] Rajendra V 1996 *Indian J Pure & Appl. Phys* 34 52
[7] Ali A, Hyder S and Nain A K 2000 *Indian J. Phys* 74B 63-7
[8] Pandey G D, Pandey S, Gupta S and Shukla A K 1994 *J. Solution Chem* 23 1049
[9] Zielkicwiz J 1998 *Chem. Soc. Faraday Trans* 94 1713
[10] Rawat M K and Sangeeta 2008 *Indian J Pure & Appl. Phys* 46 187-192
[11] Ali A, Nain A K, Kumar N and Ibhraimim M 2002 *J Pure Appl. Ultrason*. 24 27–35
[12] Oswal S L, Patel N B 2000 J. Chem. Eng. Data 45 225-230

[13] Saravanakumar K, Baskaran R and Kubendran T R 2012 Russian Journal of physical Chemistry A 86 1947-52

[14] Peralta R D, Infante R, Cortez G, Angulo J L and Wisniak J 2002 Physics and Chemistry of Liquids 40 649–60.

[15] Naidu B V K, Rao K C and Subha M C S 2003 J. Chem. Eng. Data 48 625-27.

[16] Gupta M and Shukla J P 1996 Indian J Pure Appl. Phys 34 769-72.

[17] Pandey J D, Rai R D, Shukla A K and Mishra N 1993 Indian J pure Appl. Phys 31 84- 91

[18] Pankaj and Sharma C 1991 Ultrasonics 29 344-7.

[19] Velmourougane S, Nambinarayanan T K, Rao A S and Krishnan K 1987 Indian J Phys., 61B 105-9.

[20] Sun T and Teja A S 2003 J. Chem. Eng. Data 48 198-203.

[21] Flasinski M, Gawrys M, Broniatowski M and Wydro P 2016 Biochim. Biophys. Acta 1858 836–44.

[22] Soni M G, Carabin I G and G.A. Burdock 2005 Food Chem. Toxicol 43 985-1015.

[23] Chimankar O P, Shriwas R S, Chopde P S, Tabhane V A 2011 J Chem Pharm Res 3 579-86.

[24] Balamurugan K, Shanmugam N, Palanveil R 2009 Recent Res. Sci. Technol 1 291-3.