Investigations on the interactions in the Binary Mixtures of Tripropylene Glycol Monomethyl Ether (TPGMME) and 1-Heptanol at Different Temperatures

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Abstract. Densities (ρ) and ultrasonic speeds (u) of the binary liquid mixtures of Tripropylene Glycol Monomethyl Ether (TPGMME) and 1-heptanol have been measured as a function of composition at temperature range of 288.15 to 318.15 K and atmospheric pressure. The measurements have been carried out using an Anton Paar density and speed of sound analyser DSA 5000. Thermodynamic properties like excess molar volumes, isentropic compressibility and molar isentropic compressibility have been calculated by using densities and speed of sound data at various temperatures. Value for excess molar volume is positive for (TPGMME) and 1-heptanol over the entire mole fraction range, and increase with increasing temperature.

1. Introduction
Thermodynamics parameters of a mixture including ethers and alcohols are vital importance in petroleum-based applications such as the design of heat exchangers; reactors and fluid phase separations equipment modelling and [1]. To understand the molecular interactions occurring between the binary mixtures we have to collect the experimental information such as the speed of sound, density. Another important application of thermodynamic data is the transformation of macroscopic data of a system into related data for that system through certain mathematical relation. Physico-chemical properties such as density, speed of sound are helpful to design different types of structural interactions and to recognize different thermodynamic parameters. To understand the different types of pattern between the binary mixtures of alcohols and ethers, we have to recognise the molecular interactions. A binary mixture of alkoxypyropanol and 1-alkanols generate properties due to their complexity of structure, specific interaction of molecules, and different types of hydrogen bonds present in the molecule's effects [5]. A binary mixture of alkoxypyropanol and 1-alkanols has fast evaporation rate and excellent ability to solubilize organic soils. Solute-solute, solute-solvent, solvent-so solvent molecular interactions are important properties to go through the deep information about structural changes and they can be understood by knowing the excess thermodynamic properties of the binary mixture. Positive values of molar volume indicate the strong interactions between ethers and alcohols. The mixture of ethers and alcohols are important because of their self-association properties which are produced by the presence of -O and -OH molecules in the same molecules [7]. Due to their miscible behaviour in the solvents, they are used as liquid cleaners, oil solvents and fuel additive. Molecular interactions present between the binary mixtures provides us with information about packing phenomena. Solutions of alcohols (refrigerant) with absorbents as alkoxylanol have been anticipated as working fluids for absorption refrigerant machines in order to improve the cycle.
machine [8]. This type of systems is used as gasoline additives due to their octane-enhancing and pollution-reducing properties [9]. To understand the nature and extent of patterns of the molecule, it is necessary to study the thermodynamic properties of binary mixture. This paper reports the measurement of density, speed of sound of the binary mixture containing TPGMME (C_{10}H_{22}O_{4}) with CH_{3}(CH_{2})_{6} OH at T = (288.15, 298.15, 308.15, 318.15) over the whole work range. From the recorded data, different types of thermodynamic parameters such as excess molar volume, deviations in isentropic compressibility K_{S}, has been calculated and reported in term of interactions between molecules of the mixture.

![Tripropylene Glycol Monomethyl Ether](image1.png)

![Heptanol](image2.png)

**Figure 1.** Structures of (a) Tripropylene Glycol Monomethyl Ether (b) 1-Heptanol

### 2. Experimental

#### 2.1 Materials

Chemical used for our study of thermodynamic properties of binary mixture of 1-Heptanol with TPGMME (Tripropylene glycol monomethyl ether). 1-Heptanol with mass fraction purity > 0.98 was procured from S.D. Fine Chem. Ltd. Mumbai, India, while TPGMME of Sigma Aldrich with mass fraction purity > 0.97. All chemicals were obtained in their highest purity as indicated in Table 1. Freshly prepared triply distilled and degassed water (specific conductance < 10^{-6} S·cm^{-1}) was used for the preparation of solutions. The solutions were prepared by weighing on balance having precision of ± 0.00001g. The purity of solvents were further ascertained by comparing their densities, speed of sound at 298.15 K with values reported in literature [13] in table 1.

| Chemicals                        | Source              | Purification Method          | Mass Fraction Purity |
|----------------------------------|---------------------|------------------------------|----------------------|
| 1-heptanol                       | S D Fine-Chem.      | No further purification      | >0.98                |
|                                  | Limited             |                              |                      |
|                                  | Mumbai, India       |                              |                      |
| Tripropylene glycol monomethyl   | Sigma Aldrich       | No further purification      | >0.97                |
| ether                            | Germany             |                              |                      |

*as declared by supplier

#### 2.2 Apparatus and procedure

Density and speed of sound data have been recorded by using the instrument Anton Paar Density and Speed of sound analyzer i.e. DSA 5000M densimeter. Triply distilled water is being used to check the density of air/water at 293.15 K with dry air at atmospheric pressure. The speed of sound measurement was done at the frequency of 3MHz. The sensitivity of the instrument corresponds to a precision in the density and speed of sound measurements of 1×10^{-3} kg·m^{-3} and 1×10^{-2} m·s^{-1}. The standard uncertainty of the density and speed of sound estimates was found to be within ± 1 kg·m^{-3} and ± 2 m·s^{-1}, respectively. The solutions were prepared by weighing on a Sartorius CPA 225 D balance having a precision of ±0.00001g. The uncertainties in the molality of solutions are within ± 2×10^{-5} mol·kg^{-1}.
Solutions were prepared by using freshly prepared triply distilled and degassed water with the specific conductance of $<10^{-6}$ S cm$^{-1}$.

3. Result and Discussion

3.1 Densities measurements

The experimental values of densities obtained for binary mixtures of (TPGMME) tripropylene glycol monomethyl ether + 1-Heptanol at $T = (288.15, 298.15, 308.15$ and $318.15)$ K and atmospheric pressure over the whole composition range have been recorded and listed in table 2.

Table 2. Densities ($\rho$) of binary liquid mixtures of tripropylene glycol monomethyl ether (TPGMME) + 1-heptanol at different temperatures

| $x_1$     | $\rho \times 10^3$ (kg m$^{-3}$) |
|-----------|----------------------------------|
|           | $T = 288.15$ K | $T = 298.15$ K | $T = 308.15$ K | $T = 318.15$ K |
| 0.09690   | 0.825825       | 0.818818       | 0.811730       | 0.804540       |
| 0.12344   | 0.839812       | 0.832675       | 0.825458       | 0.818076       |
| 0.19451   | 0.843309       | 0.836148       | 0.828890       | 0.821460       |
| 0.25665   | 0.853508       | 0.846247       | 0.838900       | 0.831330       |
| 0.36034   | 0.862250       | 0.854903       | 0.847480       | 0.839790       |
| 0.45799   | 0.878277       | 0.870738       | 0.863105       | 0.855300       |
| 0.56793   | 0.891390       | 0.883703       | 0.875931       | 0.867990       |
| 0.64079   | 0.907417       | 0.899558       | 0.891612       | 0.883500       |
| 0.71953   | 0.919161       | 0.911138       | 0.903065       | 0.894780       |
| 0.83255   | 0.929412       | 0.921268       | 0.913051       | 0.904650       |
| 0.93113   | 0.946956       | 0.938593       | 0.930165       | 0.921570       |
| 0.98940   | 0.961706       | 0.953133       | 0.944507       | 0.935670       |
| 0.9690    | 0.969011       | 0.960358       | 0.951622       | 0.942720       |
| 0.12344   | 0.971726       | 0.963065       | 0.954342       | 0.945439       |

3.2 Excess molar volume

For the binary system of TPGMME with 1-heptanol, excess molar volumes have been calculated by operating the density values. The following relation has been used to find the values of $V_m^E$:

$$V_m^E = \{ (x_1M_1 + x_2M_2) / \rho_t \} - \{ (x_1M_1 / \rho_1) - (x_2M_2 / \rho_2) \}$$

(1)

where $x_1$ represent the mole fraction of TPGMME and $x_2$ is mole fraction of 1-heptanol, $M_1$ is the molar mass of TPGMME; $M_2$ is the molar mass of 1-heptanol; $\rho$ is the density of binary mixture and $\rho_t$ is the density of TPGMME; $\rho_1$ is the density of 1-heptanol. The uncertainties recorded for the excess molar volumes are within the range of $\pm0.0003 \times 10^3$ m$^3$-mol$^{-1}$. The values of excess molar are recorded in table 3. The positive value of excess molar volume indicates that there is weak interactions between the ether and alcohols, more the positive value lesser will be the interactions. At all the temperature the value of excess molar volume is positive. figure 1. Shows the variation of excess molar volume with molality at different temperatures.

Table 3. Excess molar volume ($V_m^E$) of binary liquid mixtures of TPGMME + 1-heptanol at different temperatures

| $x_1$     | $T = 288.15$ K | $T = 298.15$ K | $T = 308.15$ K | $T = 318.15$ K |
|-----------|----------------|----------------|----------------|----------------|
| 0.00000   | 0.000          | 0.000          | 0.000          | 0.000          |
| 0.09690   | 1.083          | 1.085          | 1.088          | 1.101          |
| 0.12344   | 1.312          | 1.313          | 1.318          | 1.334          |
| 0.19451   | 1.890          | 1.892          | 1.896          | 1.920          |
| 0.25665   | 2.280          | 2.282          | 2.285          | 2.315          |
3.3 Speed of sound measurements
The experimental values of speed of sound obtained for binary mixtures of (TPGMME) tripropylene glycol monomethyl ether + 1-heptanol at T = (288.15, 298.15, 308.15 and 318.15) K and atmospheric pressure over the whole composition range have been recorded and listed in Table 4.

| $x_1$  | T = 288.15 K | T = 298.15 K | T = 308.15 K | T = 318.15 K |
|--------|--------------|--------------|--------------|--------------|
| 0.00000| 1239.80      | 1205.66      | 1171.90      | 1138.58      |
| 0.09690| 1248.39      | 1214.16      | 1180.32      | 1146.87      |
| 0.12344| 1252.24      | 1217.98      | 1184.10      | 1150.59      |
| 0.19451| 1258.77      | 1224.44      | 1190.50      | 1156.89      |
| 0.25665| 1262.99      | 1228.62      | 1194.64      | 1160.97      |
| 0.36034| 1276.43      | 1241.93      | 1207.81      | 1173.94      |
| 0.45799| 1286.21      | 1251.62      | 1217.41      | 1183.39      |
| 0.56793| 1298.28      | 1263.57      | 1229.24      | 1195.04      |
| 0.64079| 1305.58      | 1270.80      | 1236.40      | 1202.09      |
| 0.71953| 1314.03      | 1279.17      | 1244.68      | 1210.25      |
| 0.83525| 1323.91      | 1288.95      | 1254.37      | 1219.79      |
| 0.93113| 1335.63      | 1300.55      | 1265.86      | 1231.10      |
| 0.98940| 1338.90      | 1303.80      | 1269.07      | 1234.26      |

Figure 2. Plot of Excess molar volume ($V_M^E$) of binary liquid mixtures of tripropylene glycol monomethyl ether + 1-heptanol at different temperatures
3.4 Excess molar isentropic compressibility

Newton-Laplace’s equation has been used to calculate the isentropic compressibility by using Speed of sound data.

Table 5. Values of isentropic compressibilities ($\kappa_s$) of binary liquid mixtures of TPGMME + 1-heptanol at different temperatures

| $x_1$  | $T = 288.15$ K | $T = 298.15$ K | $T = 308.15$ K | $T = 318.15$ K |
|--------|----------------|----------------|----------------|----------------|
| 0.00000 | 653.44         | 693.39         | 736.27         | 782.33         |
| 0.09690 | 644.28         | 683.83         | 726.28         | 772.08         |
| 0.12344 | 642.04         | 681.48         | 723.84         | 769.58         |
| 0.19451 | 635.61         | 674.78         | 716.84         | 762.39         |
| 0.25665 | 630.22         | 669.16         | 710.97         | 756.37         |
| 0.36034 | 620.63         | 659.18         | 700.61         | 745.66         |
| 0.45799 | 613.05         | 651.28         | 692.38         | 737.19         |
| 0.56793 | 604.09         | 641.95         | 682.66         | 727.19         |
| 0.64079 | 597.72         | 635.33         | 675.77         | 720.15         |
| 0.71953 | 592.29         | 629.69         | 669.92         | 714.14         |
| 0.83525 | 583.29         | 620.33         | 660.19         | 704.15         |
| 0.93113 | 575.97         | 612.73         | 652.31         | 696.11         |
| 0.98940 | 572.44         | 609.06         | 648.50         | 692.19         |
| 0.09690 | 571.14         | 607.64         | 647.50         | 690.70         |

\[
\kappa_s = \frac{1}{u^2} \rho = V (M u^2)^{-1}
\]  \hspace{1cm} (2)

Where $x_i$ represent mole fraction, $M_i$ represent molar mass and $\rho$ denotes density of pure component i, $\rho$ and $u$ are the density and speeds of sound of the binary mixture of TPGMME with 1-heptanol. The values of Excess molar isentropic compressibility have been listed in the table 5. All the values of excess molar isentropic compressibility are positive and increase with increase in temperature.

Figure 3. A plot of isentropic compressibilities ($\kappa_s$) of binary liquid mixtures of TPGMME + 1-heptanol at different temperatures.

The molar isentropic compressibility ($\kappa_{s,m}$) can be calculated from
\[ K_{S,m} = -(\rho V / \rho P)_s = V k_s = \Sigma x_i M_i (\rho \mu)^2 \]  

(3)

\( \rho \) denotes the density, \( V \) represents the molar mass, \( x_i \) is mole fraction and \( M_i \) is the molar mass of the components \( i \) in the binary mixture respectively. The values of \( K_{S,m} \) are listed in table 6.

**Table 6.** Values of molar isentropic compressibility of binary liquid mixtures of TPGMME + 1-heptanol at different temperatures

| \( x_1 \) | \( K_{S,m} \) (\( \text{mm}^3 \cdot \text{mol}^{-1} \cdot \text{MPa}^{-1} \)) |
|---|---|
| | \( T = 288.15 \text{ K} \) | \( T = 298.15 \text{ K} \) | \( T = 308.15 \text{ K} \) | \( T = 318.15 \text{ K} \) |
| 0.0000 | 91.9448 | 98.4018 | 105.3986 | 112.9928 |
| 0.0969 | 95.7806 | 102.5316 | 109.8492 | 117.8299 |
| 0.1234 | 96.6976 | 103.5174 | 110.9144 | 118.9890 |
| 0.1945 | 99.2812 | 106.3032 | 113.9183 | 122.2611 |
| 0.2566 | 101.3922 | 108.5811 | 116.3760 | 124.9418 |
| 0.3603 | 110.9401 | 115.5143 | 123.8933 | 133.1186 |
| 0.4579 | 107.7956 | 112.5182 | 120.6472 | 129.5773 |
| 0.5679 | 110.9401 | 118.2241 | 127.5917 | 137.1631 |
| 0.6407 | 113.0532 | 121.2261 | 130.0951 | 139.9219 |
| 0.7195 | 114.8098 | 123.1377 | 132.1842 | 142.2175 |
| 0.8352 | 117.6285 | 126.2129 | 135.5406 | 145.9125 |
| 0.9311 | 119.7656 | 128.5568 | 138.1105 | 148.7757 |
| 0.9894 | 120.7943 | 129.6799 | 139.3469 | 150.1382 |

Experimental data of \( \rho \) and \( u \) are used to calculate molar isentropic compressibility \( (K_{S,m}^E) \) by using the following equation

\[ K_{S,m}^E = K_{S,m} - K_{S,m}^{id} \]  

(4)

\[ K_{S,m}^{id} = \sum_i [(K^*_{si} - \sum_k A^*_p / C^*_p (A^*_p/C^*_p)) ] \]  

(5)

Where \( A^*_p \) (\( V_{m*} \) \( \alpha_p^* \)) represent the product of molar volume and isobaric expansibility, \( C_p^* \) is molar isobaric heat capacity, \( K^*_{ai} \) is the product of molar volume \( V_{m*} \) and the isentropic

**Figure 4.** Plot of molar isentropic compressibilities of binary liquid mixtures of TPGMME + 1-heptanol at different temperatures
compressibility $K_{s,i}^a$ of the pure liquid component $i$. The value of $K_{s,m}^E$ is negative over the whole range of mole fraction at all temperatures listed in Table 7.

**Table 7.** Values of excess molar isentropic compressibilities of binary liquid mixtures of tripropylene glycol monomethyl ether + 1-heptanol at different temperatures

| $x_1$ | $T = 288.15$ K | $T = 298.15$ K | $T = 308.15$ K | $T = 318.15$ K |
|-------|----------------|----------------|----------------|----------------|
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.09690 | -1.01 | -1.06 | -1.10 | -1.17 |
| 0.12344 | -1.22 | -1.28 | -1.33 | -1.42 |
| 0.19451 | -1.75 | -1.83 | -1.90 | -2.02 |
| 0.25665 | -2.10 | -2.20 | -2.27 | -2.43 |
| 0.36034 | -2.51 | -2.64 | -2.73 | -2.90 |
| 0.45799 | -2.64 | -2.77 | -2.86 | -3.04 |
| 0.56793 | -2.56 | -2.69 | -2.76 | -2.94 |
| 0.64079 | -2.33 | -2.46 | -2.51 | -2.69 |
| 0.71953 | -2.04 | -2.15 | -2.19 | -2.36 |
| 0.83525 | -1.35 | -1.43 | -1.42 | -1.56 |
| 0.93113 | -0.57 | -0.62 | -0.55 | -0.69 |
| 0.98940 | -0.13 | -0.16 | -0.08 | -0.18 |
| 0.09690 | 0.00 | 0.00 | 0.00 | 0.00 |

With increase in temperature, the magnitude of $K_{s,m}^E$ decreases for a binary mixture of TPGMME+ 1-heptanol. As we increased the number of carbon atom in the alkyl chain of the alkanol molecule, the magnitude of $K_{s,m}^E$ increase. Less compressibility of mixture corresponding to the ideal mixture is indicated by the negative values of $K_{s,m}^E$, this will suggest that there may be breaking off the hydrogen-bonded structure of alcohol by TPGMME, which results in a denser packing. As we
increased the temperature, the attractive forces between the two liquid components i.e. alcohol and ethers increases which result in the more negative values for $K_{3,m}^E$.

4. Conclusion
The molecular interactions between binary mixtures of (TPGMME) and 1-Heptanol have studied by thermodynamic attitude. Our work is related to the study of mixtures covering tripropylene glycol monomethyl ether + 1-heptanol at different concentrations for the investigation and understanding of the thermodynamic parameters. To understand the nature and extent of the arrangements of molecular combination that exists in binary mixtures of alcohols and ethers we have to understand the apparent thermodynamic properties, which depend on the composition, temperature and pressure, are of great importance in helping. In this work, an examination has been made of some of the graphical and analytical perspectives of the thermodynamic data that have been taken for the mixtures. In conclusions, it is fair to ask whether we are any closer to any understanding of the nature of the patterns of molecular interactions which exist within such mixtures. Our study only indicates that we are still in the dark regarding the proper elucidation of different types of interactions that occur in the molecule. The data obtained from the binary mixture and the thermodynamic parameters provide vital information about the structural changes and the different types of molecular

Figure 6. Schematic diagram indicating the solute solvent interactions between TPGMME and 1-heptanol.

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Acknowledgements
This work is supported by Science and Engineering Research Board (SERB), New Delhi through sanction order number EMR/2015/002059. Authors are thankful to the Director and Head, Department of Chemistry, Dr B. R. Ambedkar National Institute of Technology, Jalandhar, for providing MHRD fellowship (Ravinder Sharma) and essential laboratory facilities.