

Study of Molecular Interactions in Stearates and Triethylene Glycol through Ultrasonic Measurements

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Abstract:- Speed of sound have been measured as a function of composition for binary mixtures of stearates (zinc stearate and calcium stearate) and triethylene glycol were studied along with density and viscosity values, a comprehensive understanding of the molecular interactions in the binary mixture is thus only possible from the measurements of various physico – chemical properties and treating the excess functions derived there from [1]. In spite of this interesting consideration, the concrete studies on the excess functions of zinc stearate – triethylene glycol and calcium stearate – triethylene glycol mixtures are studied. The results have been discussed in terms of molecular interactions. The aim of this work was also to find out if there are any structural peculiarities in solutions of stearate and glycol.

Keywords:- Glycol, Stearate, Stabilizer, Plasticizer

I. INTRODUCTION

The study of molecular interaction in the solid - liquid mixtures is of considerable importance in the elucidation of the structural properties of the molecules. The intermolecular interactions influence the structural arrangement along with the shape of the molecules. The components capable of undergoing specific interaction exhibit significant deviation from ideal behaviour, arising not only from the difference in molecular size and shape but also due to the structural changes. Ultrasonic methods has the added advantage of being less costly with efficiency comparable to other methods. Volumetric properties of binary mixtures are complex properties because they depend not only on solute - solute, solute - solvent and solute - solvent interactions, but also of the structural effects arising from interstitial accommodation due to the difference in molar volume and free volume between components present in the solution [2]. Moreover, there is interest in using volumetric data to test molecular theories or models of solution to extend our understanding about molecular interaction between components [3]. The values of ultrasonic velocity (U), density (ρ) and viscosity (η) for the pure components is given in Table 1. From the experimental values, a few acoustical parameters such as adiabatic compressibility (B), acoustical impedance (Z), molar sound velocity (R), Wada's constant (W), molar volume (Vm), free volume (Vf), intermolecular free length (Lf), internal pressure (π), absorption coefficient (α/f^2) viscous relaxation time (τ), degree of intermolecular attraction (α), excess ultrasonic velocity (UE), excess adiabatic compressibility (BE), excess acoustical impedance (ZE), excess free length (LfE) and excess molar volume (VmE) were derived over the entire mole fraction range. Ultrasonic velocities have also been evaluated theoretically with the help of Impedance relation, Nomoto relation, Van Dael & Vangeel relation and Junjie relation. The suitability of these theories and equations were checked by comparing theoretical values of ultrasonic speeds with the values obtained experimentally. Literature survey showed that no measurements have been previously reported for the mixtures reported in this paper [4].

II. MATERIALS AND METHODS

The chemicals used were of analytical grade and obtained from E.Merck company. Thermostatically controlled well-stirred water bath whose temperature was maintained to ± 0.01 K accuracy was used for all the measurements. Binary mixtures were prepared by weighing in airtight bottles, the possible uncertainty in the concentration is estimated to be less than ± 0.0001 . Densities of pure components and their mixtures were determined by using a 1×10^{-5} m³ double arm pycnometer. The density values from triplicate replication at the temperature of 303 K were reproducible within $\pm 2 \times 10^{-2}$ kg m⁻³. The uncertainty in density and excess molar volume values were found to be $\pm 4 \times 10^{-2}$ kg m⁻³ and $\pm 0.001 \times 10^{-6}$ m³ mol⁻¹ respectively. Ostwald's viscometer having capacity of about 15 ml and the capillary having a length of about 90 mm and 0.5 mm internal diameter has been used to measure the flow times of pure liquids and liquid mixtures and it was calibrated with benzene (density ≈ 0.8738 g cm⁻³) and doubly distilled water (density ≈ 0.9970 g cm⁻³) at 303 K. The flow time of pure liquids and liquid mixtures were repeated for five times. The uncertainty of viscosity

was $\pm 0.005 \times 10^{-3}$ m Pas. Speed of sound was measured by using a variable path, single crystal interferometer. (United scientific company, India), working at 2 MHz frequency. The interferometer was calibrated using toluene. Measurement of speed of sound through medium was based on the accurate determination of the wavelength of ultrasonic waves of known frequency produced by quartz crystal in the measuring cell. The interferometer cell was filled with the test liquid, and water was circulated around the measuring cell from a thermostat. The uncertainty was estimated to be 0.1ms⁻¹.

The adiabatic compressibility (β_s) was calculated by the equation

$$\beta = 1/\rho U^2 \quad (1)$$

Where ρ is the density of mixture and U is the ultrasonic velocity of the mixture.

The acoustical impedance (Z) was calculated by the equation,

$$Z = \rho U \quad (2)$$

Where ρ is the density of mixture and U is the ultrasonic velocity of the mixture.

The molar sound velocity (R) was calculated by the equation

$$R = (M_{eff}/\rho) U^{1/3} \quad (3)$$

Where U is the ultrasonic velocity of the mixture.

The molar compressibility or Wada's constant (W), was calculated by the equation

$$W = (M/\rho) \beta^{-1/7} \quad (4)$$

Where M is the relative molar mass and β is the adiabatic compressibility.

The intermolecular free length (L_f) was calculated by the equation

$$L_f = k \beta^{1/2} \quad (5)$$

Where $K = 1.98 \times 10^{-6}$, the Jacobson constant (Jacobson 1952).

The Free volume was calculated by the equation

$$V_f = (M_{eff} U / K \eta)^{3/2} \quad (6)$$

Where $K = 4.28 \times 10^9$ for all liquids which is a temperature independent constant.

The internal pressure was calculated by the equation

$$\pi = \{bRT / (V^2 V_f)\}^{1/3} \quad (7)$$

b is a packing factor, R is a gas constant, V_f is free volume and T is temperature.

The absorption coefficient was calculated by the equation

$$(\alpha/f^2) = (8\pi^2\eta/3\rho U^3) \quad (8)$$

η is viscosity of the mixture and ρ is the density of the mixture.

The viscous relaxation time was calculated by the equation

$$\tau = (4\eta/3\rho U^2) \quad (9)$$

η is viscosity of the mixture and ρ is the density of the mixture.

The degree of intermolecular attraction (α) was calculated by the equation

$$\alpha = (u^2 / u_{2im}) - 1 \quad (10)$$

Where $u_{2im} = 1 / \{(x_1 M_1 + x_2 M_2)(x_1 / M_1 u_1^2 + x_2 / M_2 u_2^2)\}$

The U_E , β_E , Z_E , L_{fE} , and V_{mE} were derived over the entire mole fraction range by using the general equation

$$A_E = A - (X_i A_1 + (1-X_i) A_2) \quad (11)$$

Where A is the corresponding parameters (U , β , Z , L_f , and V_m) of binary mixture and A_1 and A_2 are the corresponding pure component values.

The sound velocity can be correlated with the relation called Impedance relation which is represented as UIMR

$$= (X_1 Z_1 + X_2 Z_2) / (X_1 \rho_1 + X_2 \rho_2) \quad (12)$$

where X , Z , ρ denote the mole fraction, acoustic impedance and density of the component respectively.

Nomoto derived an empirical formula for the sound velocity in binary mixture. It is given by the equation

$$U_{IMR} = \left\{ \frac{[1/(X_1 M_1 + X_2 M_2)]}{[X_1/M_1 U_1^2 + X_2/M_2 U_2^2]} \right\}^{1/2} \quad (13)$$

Where X , R , V denote the mole fraction, molar sound velocity and

molar volume at temperature T of the component. The acoustical behaviour of binary mixture was studied in detail by Van Dael et al. The expression for sound velocity (U_{imr}) of binary mixtures can be obtained from equation

$$U_{imr} = \left\{ \frac{(X_1 V_1 + X_2 V_2)}{(X_1 M_1 + X_2 M_2)^{1/2}} \left[\frac{X_1 V_1}{\rho_1 u_1^2} + \frac{X_2 V_2}{\rho_2 u_2^2} \right] \right\}^{-1/2} \quad (14)$$

Where X, M and U are the mole fraction, molecular weight and sound velocity of component. Junjie derived an empirical formula for the sound velocity in binary mixture. It is given by the equation

$$U_{\text{jun}} = \left\{ \frac{(X_1 V_1 + X_2 V_2)}{(X_1 M_1 + X_2 M_2)^{1/2}} \left[\frac{X_1 V_1}{\rho_1 U_1^2} + \frac{X_2 V_2}{\rho_2 U_2^2} \right] \right\}^{-1/2} \quad (15)$$

Where X, V, M, ρ denote the mole fraction, molar volume, molecular weight and density of the components. The percentage deviation of the experimental velocity from the theoretical value is given by the equation

$$\text{Percentage deviation in velocity} = \frac{U_{\text{Theo}} - U_{\text{Expt}}}{U_{\text{Theo}}} \times 100 \quad (16)$$

III. RESULTS AND DISCUSSION

The ultrasonic velocity, density and viscosity data for the pure components at 303 K are given below:

Table 1 Comparison of density, ultrasonic velocity and viscosity data at 303 K

| Component | U m/s | ρ Kg/m ³ | $\eta \times 10^{-1}$ Nsm ⁻² |
|--------------------|----------|-----------------------------|--|
| Zinc stearate | 1404 | 1133 | - |
| Calcium stearate | 1310 | 1145 | - |
| Triethylene glycol | 1912 | 1100 | 22.4 |

Table 2 gives the measured and acoustic parameters such as ultrasonic velocities (U), density (ρ), viscosity (η), adiabatic compressibility (β), acoustical impedance (Z), molar sound velocity (R), molar compressibility (W), molar volume (Vm), free volume (Vf), Table 3 gives the thermodynamic properties like intermolecular free length (Lf), internal pressure (π), absorption coefficient (α/f^2), viscous relaxation time (τ), degree of intermolecular attraction (α), Table 4 gives the excess parameters like excess ultrasonic velocity (UE), excess adiabatic compressibility (βE), excess acoustical impedance (ZE), excess free length (Lfe), excess molar volume (VmE), Table 5 gives the theoretical values of ultrasonic velocity calculated from Impedance, Nomoto, Van Dael & Vangeel and Junjie's relation along with the experimental ultrasonic velocity and percentage deviation for the binary mixtures zinc stearate - triethylene glycol and calcium stearate - triethylene glycol over the entire composition range at 303 K.

Table 2 : Measured and acoustic parameters of binary mixtures at 303 K

| Conc of stearate | U ms ⁻¹ | ρ Kgm ⁻³ | $\eta /$ Nsm ⁻² | $\beta / 10 \cdot 10$ Kg ⁻¹ ms ⁻² | Z / 106 Kg m ⁻² s ⁻¹ | R | W | Vm / 10 ⁻¹ m ³ mole ⁻¹ | Vf / 10 ⁻⁸ m ³ mole ⁻¹ |
|------------------------------------|-----------------------|-----------------------------|-------------------------------|--|---|------|------|--|--|
| zinc stearate – triethylene glycol | | | | | | | | | |
| 0.01 | | 1106.3 | | | | | | | |
| | 1920 | 2 | 23.6 | 2.45 | 2.12 | 1.69 | 3.22 | 1.36 | 0.486 |
| 0.02 | | 1112.6 | | | | | | | |
| | 1976 | 4 | 24.2 | 2.30 | 2.20 | 1.71 | 3.24 | 1.36 | 0.492 |
| 0.03 | | 1118.9 | | | | | | | |
| | 1996 | 6 | 24.5 | 2.24 | 2.23 | 1.71 | 3.25 | 1.36 | 0.494 |
| 0.04 | | 1125.2 | | | | | | | |
| | 2064 | 8 | 25.0 | 2.09 | 2.32 | 1.73 | 3.28 | 1.36 | 0.506 |
| 0.05 | | 1131.6 | | | | | | | |
| | 2124 | 1131.6 | 25.3 | 1.96 | 2.40 | 1.74 | 3.30 | 1.36 | 0.523 |
| 0.06 | | 1137.9 | | | | | | | |
| | 2224 | 2 | 25.5 | 1.78 | 2.53 | 1.77 | 3.35 | 1.35 | 0.555 |
| 0.07 | | 1144.2 | | | | | | | |
| | 2256 | 4 | 25.7 | 1.72 | 2.58 | 1.77 | 3.36 | 1.35 | 0.564 |
| 0.08 | | 1150.5 | | | | | | | |
| | 2376 | 6 | 26.1 | 1.54 | 2.73 | 1.80 | 3.41 | 1.35 | 0.602 |
| 0.09 | | 1156.8 | | | | | | | |
| | 2420 | 8 | 26.3 | 1.48 | 2.80 | 1.81 | 3.42 | 1.35 | 0.616 |
| 0.1 | | 1163.2 | | | | | | | |
| | 2808 | 1163.2 | 26.5 | 1.09 | 3.27 | 1.90 | 3.57 | 1.35 | 0.764 |

| calcium stearate – triethylene glycol | | | | | | | | | |
|---------------------------------------|------|--------|------|------|------|------|------|------|-------|
| 0.01 | | 1106.0 | | | | | | | |
| | 1928 | 4 | 24.1 | 2.43 | 2.13 | 1.70 | 3.22 | 1.36 | 0.472 |
| 0.02 | | 1112.1 | | | | | | | |
| | 1938 | 2 | 24.4 | 2.39 | 2.16 | 1.70 | 3.22 | 1.36 | 0.472 |
| 0.03 | | 1118.2 | | | | | | | |
| | 1976 | 8 | 24.7 | 2.29 | 2.21 | 1.71 | 3.24 | 1.36 | 0.480 |
| 0.04 | | 1124.2 | | | | | | | |
| | 2000 | 8 | 24.9 | 2.22 | 2.25 | 1.71 | 3.25 | 1.36 | 0.483 |
| 0.05 | | 1130.3 | | | | | | | |
| | 2032 | 2 | 25.2 | 2.14 | 2.30 | 1.72 | 3.26 | 1.36 | 0.489 |
| 0.06 | | 1136.4 | | | | | | | |
| | 2088 | 8 | 25.5 | 2.02 | 2.37 | 1.73 | 3.29 | 1.35 | 0.505 |
| 0.07 | | 1142.4 | | | | | | | |
| | 2292 | 8 | 25.7 | 1.67 | 2.62 | 1.78 | 3.37 | 1.35 | 0.577 |
| 0.08 | | 1148.5 | | | | | | | |
| | 2345 | 6 | 25.9 | 1.58 | 2.69 | 1.79 | 3.39 | 1.35 | 0.595 |
| 0.09 | | 1154.6 | | | | | | | |
| | 2375 | 8 | 26.2 | 1.54 | 2.74 | 1.80 | 3.40 | 1.35 | 0.600 |
| 0.1 | | 1160.6 | | | | | | | |
| | 2420 | 8 | 26.3 | 1.47 | 2.81 | 1.81 | 3.42 | 1.35 | 0.615 |

Table 3 : Thermodynamic parameters of binary mixtures at 303 K

| Conc of stearate | Lf / 10-11 m | π / 106 atm | α/f_2 / 10-11 m-1s2 | τ / 10-9 s | α / 10-1 m |
|---------------------------------------|--------------|-----------------|----------------------------|-----------------|-------------------|
| zinc stearate – triethylene glycol | | | | | |
| 0.01 | 3.11 | 11.2 | 7.92 | 7.71 | 0.120 |
| 0.02 | 3.01 | 11.2 | 7.40 | 7.42 | 0.758 |
| 0.03 | 2.97 | 11.2 | 7.23 | 7.32 | 1.02 |
| 0.04 | 2.87 | 11.0 | 6.65 | 6.96 | 1.82 |
| 0.05 | 2.78 | 11.0 | 6.13 | 6.60 | 2.56 |
| 0.06 | 2.64 | 10.8 | 5.36 | 6.05 | 3.82 |
| 0.07 | 2.60 | 10.7 | 5.15 | 5.89 | 4.27 |
| 0.08 | 2.46 | 10.5 | 4.44 | 5.35 | 5.88 |
| 0.09 | 2.41 | 10.5 | 4.21 | 5.17 | 6.53 |
| 0.1 | 2.07 | 9.74 | 2.70 | 3.85 | 12.3 |
| calcium stearate – triethylene glycol | | | | | |
| 0.01 | 3.09 | 11.3 | 8.00 | 7.83 | 0.203 |
| 0.02 | 3.07 | 11.3 | 7.91 | 7.77 | 0.345 |
| 0.03 | 3.00 | 11.3 | 7.51 | 7.53 | 0.792 |
| 0.04 | 2.96 | 11.3 | 7.29 | 7.40 | 1.09 |
| 0.05 | 2.90 | 11.2 | 7.00 | 7.21 | 1.49 |
| 0.06 | 2.82 | 11.1 | 6.48 | 6.86 | 2.17 |
| 0.07 | 2.56 | 10.7 | 4.91 | 5.71 | 4.72 |
| 0.08 | 2.50 | 10.6 | 4.59 | 5.46 | 5.46 |
| 0.09 | 2.46 | 10.5 | 4.45 | 5.36 | 5.91 |
| 0.1 | 2.41 | 10.5 | 4.21 | 5.17 | 6.57 |

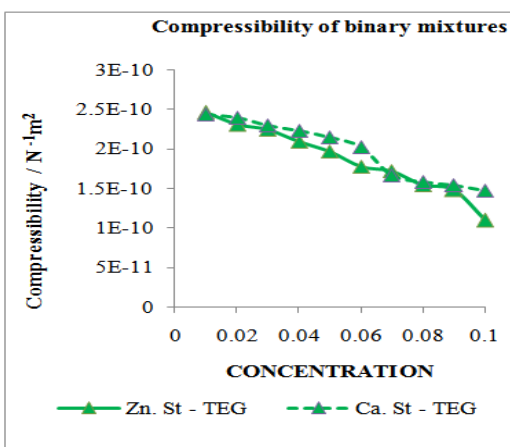
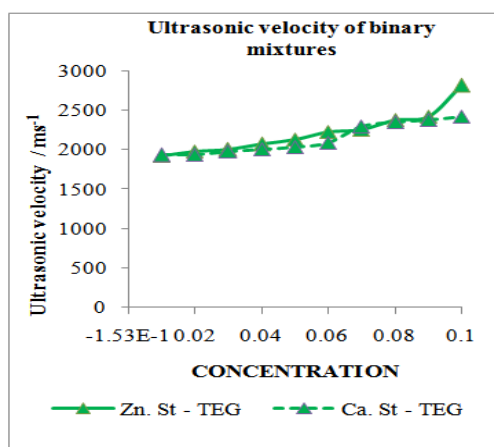
Table 4 : Excess parameters of binary mixtures like UE, βE , ZE, LfE and vmE at 303 K

| Conc of stearate | UE ms-1 | βE / 10-11 Kg-1ms-2 | ZE / 105 Kg m-2s-1 | LfE / 10-12 m | VmE / 10-3 m3mole-1 |
|------------------------------------|---------|----------------------------|--------------------|---------------|---------------------|
| zinc stearate – triethylene glycol | | | | | |
| 0.01 | 9 | -0.375 | 0.216 | -0.234 | -0.760 |
| 0.02 | 65 | -1.90 | 0.968 | -1.21 | -1.52 |
| 0.03 | 86 | -2.52 | 1.32 | -1.62 | -2.28 |
| 0.04 | 155 | -4.12 | 2.22 | -2.69 | -3.03 |
| 0.05 | 215 | -5.41 | 3.04 | -3.59 | -3.78 |
| 0.06 | 316 | -7.26 | 4.32 | -4.93 | -4.53 |
| 0.07 | 349 | -7.88 | 4.83 | -5.39 | -5.28 |
| 0.08 | 469 | -9.69 | 6.36 | -6.79 | -6.03 |

| | | | | | |
|---------------------------------------|-----|--------|-------|--------|--------|
| 0.09 | 514 | -10.3 | 7.03 | -7.31 | -6.77 |
| 0.1 | 903 | -14.2 | 11.7 | -10.7 | -7.51 |
| calcium stearate – triethylene glycol | | | | | |
| 0.01 | 17 | -0.580 | 0.301 | -0.363 | -0.719 |
| 0.02 | 28 | -0.997 | 0.537 | -0.625 | -1.44 |
| 0.03 | 66 | -2.07 | 1.09 | -1.32 | -2.16 |
| 0.04 | 91 | -2.77 | 1.49 | -1.77 | -2.88 |
| 0.05 | 124 | -3.62 | 1.98 | -2.34 | -3.59 |
| 0.06 | 181 | -4.89 | 2.75 | -3.21 | -4.30 |
| 0.07 | 386 | -8.45 | 5.21 | -5.80 | -5.02 |
| 0.08 | 440 | -9.32 | 5.97 | -6.47 | -5.73 |
| 0.09 | 470 | -9.83 | 6.46 | -6.87 | -6.43 |
| 0.1 | 516 | -10.5 | 7.14 | -7.40 | -7.14 |

Table 5 Experimental velocities and theoretical velocities along with the percentage deviation of binary mixtures at 303 K

| Conc of stearate | Ultrasonic velocity U / ms ⁻¹ | | | | Junjie's | % Deviation | | | |
|---------------------------------------|--|------|------|------|----------|-------------|---------|---------|----------|
| | EXPT | Imp | Nom | VDV | | Imp | Nom | VDV | Junjie's |
| zinc stearate – triethylene glycol | | | | | | | | | |
| 0.01 | 1920 | 1911 | 1909 | 1909 | 1908 | -0.456 | -0.582 | -0.599 | -0.650 |
| 0.02 | 1976 | 1911 | 1906 | 1905 | 1903 | -3.424 | -3.683 | -3.719 | -3.820 |
| 0.03 | 1996 | 1910 | 1903 | 1902 | 1899 | -4.510 | -4.899 | -4.954 | -5.105 |
| 0.04 | 2064 | 1909 | 1900 | 1898 | 1895 | -8.110 | -8.644 | -8.721 | -8.924 |
| 0.05 | 2124 | 1908 | 1897 | 1895 | 1891 | -11.294 | -11.977 | -12.077 | -12.334 |
| 0.06 | 2224 | 1908 | 1894 | 1892 | 1887 | -16.577 | -17.430 | -17.557 | -17.873 |
| 0.07 | 2256 | 1907 | 1891 | 1889 | 1883 | -18.298 | -19.302 | -19.453 | -19.821 |
| 0.08 | 2376 | 1906 | 1888 | 1885 | 1879 | -24.636 | -25.839 | -26.021 | -26.456 |
| 0.09 | 2420 | 1906 | 1885 | 1882 | 1875 | -26.990 | -28.361 | -28.572 | -29.061 |
| 0.1 | 2808 | 1905 | 1883 | 1879 | 1871 | -47.405 | -49.163 | -49.436 | -50.054 |
| calcium stearate – triethylene glycol | | | | | | | | | |
| 0.01 | 1928 | 1911 | 1908 | 1909 | 1907 | -0.882 | -1.025 | -1.012 | -1.124 |
| 0.02 | 1938 | 1910 | 1905 | 1905 | 1901 | -1.450 | -1.738 | -1.713 | -1.936 |
| 0.03 | 1976 | 1909 | 1901 | 1902 | 1896 | -3.486 | -3.924 | -3.886 | -4.223 |
| 0.04 | 2000 | 1909 | 1898 | 1899 | 1891 | -4.789 | -5.378 | -5.328 | -5.778 |
| 0.05 | 2032 | 1908 | 1895 | 1896 | 1886 | -6.513 | -7.256 | -7.193 | -7.758 |
| 0.06 | 2088 | 1907 | 1891 | 1892 | 1881 | -9.496 | -10.409 | -10.333 | -11.022 |
| 0.07 | 2292 | 1906 | 1888 | 1889 | 1876 | -20.247 | -21.411 | -21.315 | -22.187 |
| 0.08 | 2345 | 1905 | 1884 | 1886 | 1871 | -23.082 | -24.436 | -24.327 | -25.334 |
| 0.09 | 2375 | 1904 | 1881 | 1883 | 1866 | -24.711 | -26.246 | -26.123 | -27.258 |
| 0.1 | 2420 | 1904 | 1878 | 1880 | 1862 | -27.130 | -28.859 | -28.723 | -29.993 |



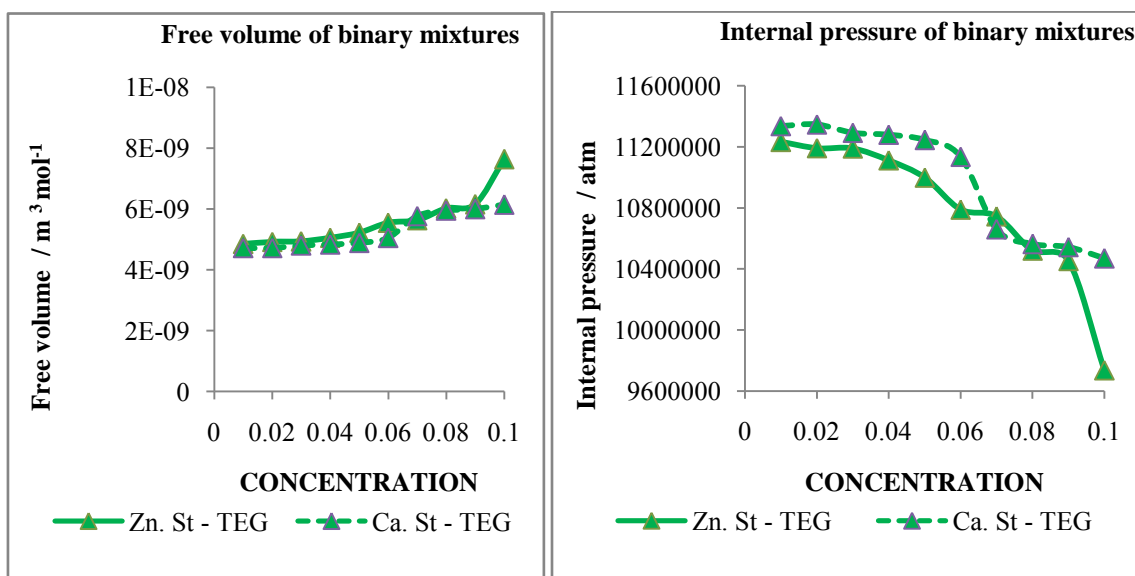


Fig.1 : Computed parameters of zinc stearate – triethylene glycol and calcium stearate – triethylene glycol

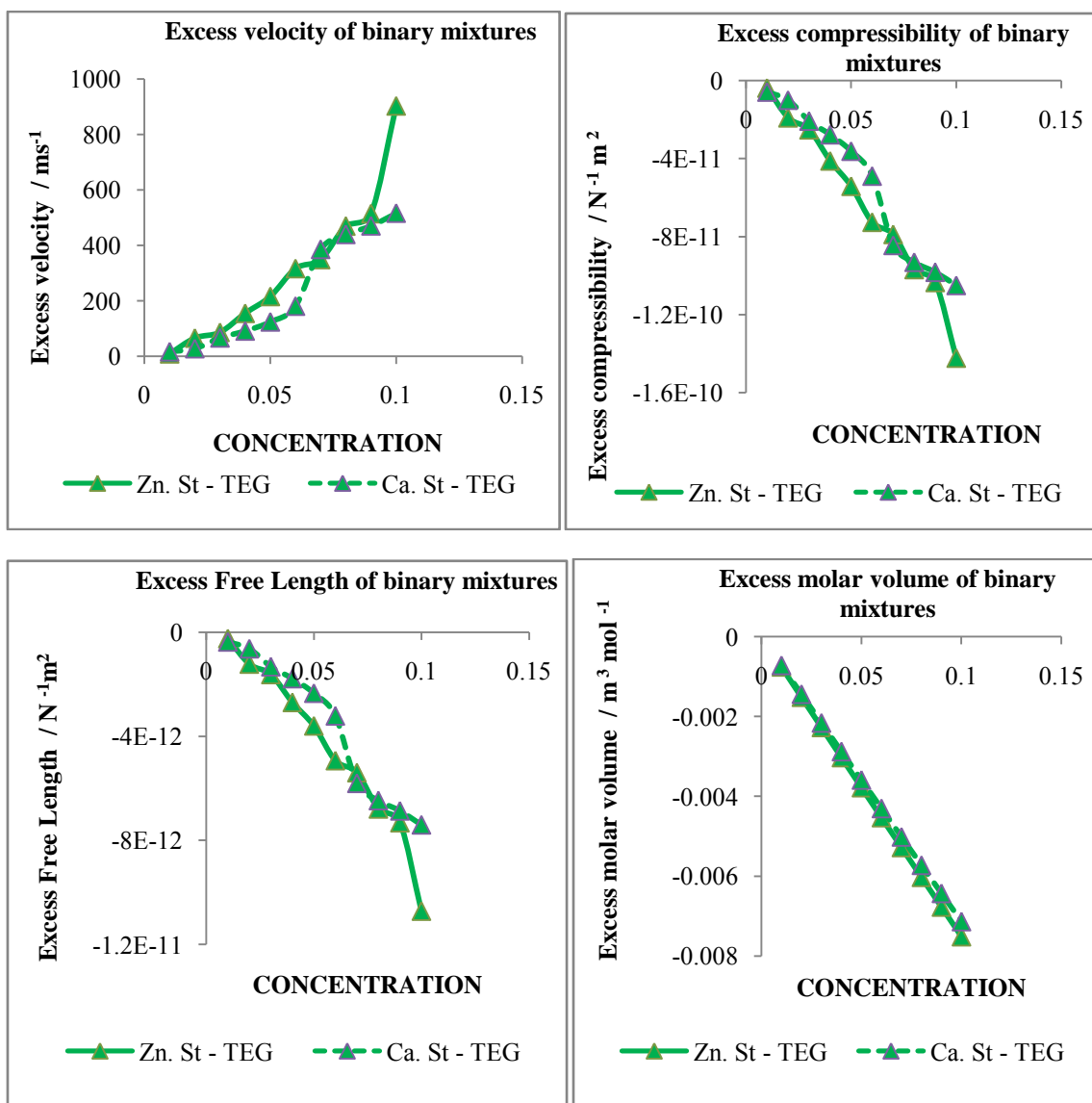


Fig.2 : Excess parameters of zinc stearate – triethylene glycol and calcium stearate – triethylene glycol

In the present investigations, studies are made with two structurally different stabilizers such as zinc stearate, calcium stearate and plasticizer triethylene glycol. Glycol finds widespread application in automotive, aviation, explosive, textile, surface coating, food, cosmetic, pharmaceutical, tobacco, petroleum, and other industries [5]. Glycols are polar and it is able to form three - dimensional network of hydrogen bonds with its neighbouring group. Strong association of glycol molecules is the reason of its relatively high temperature of melting and that of boiling as well as of its high viscosity, typical of polyhydroxyl alcohols. The ultrasonic studies on hydrogen bonding of stabilizers with plasticisers are important to understand the solute-solvent interactions at molecular level and bonding around the solute molecules.

In Zn. St – TEG and Ca. St – TEG systems, ultrasonic velocity values increases with increase in stearate concentration. The increase in ultrasonic velocity in any solution indicates the greater association among the molecules of a solution which is due to the intermolecular hydrogen bonding between the solute and the solvent molecules. The ultrasonic and computational studies on intermolecular association exist through hydrogen bonding between stabilizers and plasticizers. This is due to the presence of ester group in stabilizers and two hydroxyl groups in glycol molecules of plasticizer. The gradual increase of sound absorption with glycol concentration strongly supports the intermolecular association through hydrogen bonding between the solute and solvent molecules. Hence, as the sound wave passes, more sound energy has to be utilized to break the large number of intermolecular hydrogen bonds [6]. This predicts that components used in this present investigation are aliphatic in nature, so the interaction between aliphatic molecules is less when compared with interaction between aliphatic – aromatic molecules. It also identifies the presence of solute - solvent type of interaction between the contributing molecules [7]. The forces responsible for these interactions may be probably dipole – induced dipole or hydrogen bonding between alcoholic group of plasticizer and ester group of stabilizer. Stearates are metal soaps that are immiscible in polar solvents such as glycols. However, by passing high frequency mechanical waves in binary mixtures, it favours mixing of two components to small extent leading to less interaction. It is observed addition of zinc stearate shows maximum interaction than calcium stearate. The density values (ρ) increases with increase in stearate concentration and viscosity values (η) increases with increase in stearate concentration.

The adiabatic compressibility (β) decreases with increase in stearate concentration for both Zn. St – TEG and Ca. St – TEG systems. The change in adiabatic compressibility indicates that there is definite contraction on mixing [8]. The decrease in adiabatic compressibility brings the molecules to a closer packing resulting in decrease of free length. Further, it strengthens the strong molecular association between the unlike molecules through hydrogen bonding. Acoustic impedance (Z) increases linearly in both Zn. St – TEG and Ca. St – TEG systems, confirms the presence of molecular association between stearate - glycol molecules through intermolecular hydrogen bonding [9]. Rao's constant (R) and Wada's constant (W) shows linear variation for the binary mixtures Zn. St – TEG and Ca. St – TEG systems predicting the absence of complex formation and only weak interaction exists in all these cases. Molar volume (V_m) values remain constant for the binary mixture Zn. St – TEG and Ca. St – TEG systems. The variation of free volume (V_f) increases with increase in stearate concentration for Zn. St – TEG, Ca. St – TEG systems, predicts that packing between two components is looser favouring weak interaction.

The intermolecular free length (L_f) also follows the same trend as that of adiabatic compressibility for Zn. St – TEG and Ca. St – TEG systems, decrease in free length with increase in stearate concentration identifies significant interaction between stearates and glycols due to which the structural arrangement is considerably affected [10]. For Zn. St – TEG, Ca. St – TEG system, internal pressure decreases with increase in stearate concentration, confirms the existence of weak interaction. The absorption coefficient values (α/f^2) decreases for Zn. St – TEG and Ca. St – TEG systems with increase in stearate concentration. The values of relaxation time (τ) shows linear variation for Zn. St – TEG and Ca. St – TEG systems shows decrease trend with increase in stearate concentration. It may be due to the weakening of hydrogen bonds in TEG leading to structure breaking effect [11]. The observed value of interaction parameter (α) signifies that unlike interactions are relatively strong compared to like interactions. It is evident from the increased values of intermolecular attraction, interaction exists between unlike components and decreased values explain that the interaction occurs between like components [12]. α value increase for Zn. St – TEG and Ca. St – TEG systems, identifies the existence of interaction among them.

Non specific physical interaction and unfavourable interaction between unlike molecules and breaking of liquid order on mixing with the second component lead to expansion of volume. However specific interaction appearing in the mixture between dissimilar molecules by hydrogen bond formation or dipole – dipole interaction leads to reduction in volume. The excess velocity (UE) shows positive deviations, predicts the presence of weak interaction which may be due to dispersion force. It shows non linear variation Zn. St – TEG and Ca. St – TEG systems. It states that molecular association of the component is stronger than dissociation of the molecules. Chemical interaction leads to negative values of both excess compressibility values (β_E) and free length (L_{fE}). It also reveals the presence of interstitial accommodation between the components. Increase in

compactness between the molecules leading to solute – solvent interaction. For Zn. St – TEG and Ca. St – TEG systems, less negative deviation implies that the specific interaction may be due to structure breaking effect which dominates the dispersive interaction between unlike molecules. It indicates the existence of less molecular interaction between stabilizers and plasticizers [13]. It was reported that the positive deviation in excess impedance (ZE) indicates the presence of strong interactions between component molecules in the binary mixtures. For Zn. St – TEG and Ca. St – TEG systems shows non linear variation which identifies strong molecular interaction among them. The excess molar volume (VmE) is negative and decrease with increase in stearate concentration for entire composition range.

In binary mixtures, on mixing liquid and solid, the interactions between the molecules may take place due to the presence of various forces like dispersion forces, hydrogen bonding, dipole – dipole and dipole – induced dipole interactions. Negative deviation is observed for all the ten binary mixtures investigated and states that the mixture contains both associated and non associated components releasing more number of dipoles to form dipole – induced dipole interaction [14]. For Zn. St – TEG system, deviation follows as $U_{Jun} > U_{Vdv} > U_{Nom} > U_{Imp}$. However, for Ca. St – TEG system, deviation follows as $U_{Jun} > U_{Nom} > U_{Vdv} > U_{Imp}$. Based on the above consideration, Van Dael & Vangeel and Junjie relation shows maximum negative deviation where as Nomoto's and impedance relation are in fairly good agreement with the experimental velocity values [15].

IV. CONCLUSION

The present investigation measures ultrasonic velocity, density and viscosity of stabilizers with plasticizer at 303 K. The ultrasonic velocity data and other thermo - acoustic parameters give valuable information to understand the solute – solvent interactions in the binary mixtures. It may be suggested that the strength of interactions between aliphatic molecules are less. For Zn. St – TEG and Ca. St – TEG systems, there is a possibility of interstitial accommodation due to the different sizes of the solute and solvent molecules. In comparison among stearates, molecular interaction is greater with zinc stearate than calcium stearate. On the addition of stearate to glycols, the molecular interaction follows the order Zn. St – TEG > Ca. St – TEG

From the computed data, standard relations like Impedance relation, Nomoto relation, Van Dael and Vangeel and Junjie theory are calculated. The greater negative deviation values in Van Dael and Vangeel and Junjie relation confirm the existence of strong molecular interaction between stabilizers and plasticizer. Nomoto and Impedance relation agrees well with experimental sound velocity values.

REFERENCES

- [1]. Roshan Abraham, Abdul Khadar and Jugan J J. *Acoust. Soc. Am.*, 106(3) (1999) 1284.
- [2]. A.M. Bisdow, K.H. Ebert, *Macromol. Chem.* 176 (1975) 745.
- [3]. Rajendran V *Ind. J. Pure and Appl. Phy.*, 32 (1994) 523.
- [4]. Gokhan Savarogly, Ertunc Aral *J. Mol. Liq.*, 105/1 (2003) 79.
- [5]. Anuradha S, Prema S and Rajagopal K J. *Pure Appl. Ultrason.*, 27 (2005) 49.
- [6]. Raout B K, Mishra N C, Chakravorty V *Indian J. Chem. Technol.* 1 (1994) 347.
- [7]. Singh Y P, Das S, Maiti S and Singh R P J. *Pure Appl. Ultrason.*, 3 (1981) 1.
- [8]. Syamala V, Siva Kumar K and Vekateswarlu P J. *Mol. Liq.*, 136 (2007) 29.
- [9]. U.D. Harkal, P.R. Gogate, A.B. Pandit, M.A. Shenoy, *Ultrason. Sonochem.* 13 (2006) 423.
- [10]. Chandralekha Fadnis, Illiger S R, Rao K P, Demappa T *Carbohydrate Polymers*, 74 (2008) 779.
- [11]. R Kumar, S Jayakumar and V Kannappan., *Indian Journal of Pure & Applied Physics.*, Vol. 46. March 2008, pp. 169 – 175.
- [12]. Ulagendran, R Kumar, S Jayakumar and V Kannappan., *Journal of Molecular liquids.*, 148 (2009) pp. 67 – 72.
- [13]. R Kavitha, S Jayakumar and R Uma *ISST Journal of Applied Chemistry*, Vol.1, No.2 (2010) 57.
- [14]. R Kavitha, S Jayakumar and R Uma *IJESR*, Vol.2, Issue 4 (2011) 293.
- [15]. R Kavitha, S Jayakumar and R Uma *International Journal of Chemistry and Applications*, Vol.3, No.1 (2011) 9.