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THE ULTRASONIC STUDY OF BINARY MIXTURES ZINC STEARATE WITH PROPYLENE GLYCOL AND GLYCEROL

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Abstract:

We report the measurements of ultrasonic velocity in the binary mixtures of zinc stearate – propylene glycol and zinc stearate – glycerol at 303 K. The knowledge of the thermodynamic properties is essential in the chemical industry and used to evaluate the different thermo acoustical parameters along with the excess properties, the experimental data obtained is fitted with the models and percentage deviation is calculated. The sign, magnitude and variation in excess functions derived from physico-chemical properties reveal important information about the type of molecular interactions that are not usually seen from the variations in their excess volumes.

Key Words: Stearate, Propylene Glycol, Glycerol & Excess Functions

Introduction:

Stabilizers are the substances that are used to prevent unwanted change in state of another substance, reducing vapour pressure and stabilize the material developed. In our present investigation, zinc stearate is used as stabilizers in manufacture of biodegradable plastics. Plasticizers are additives that increase the plasticity or fluidity of the material to which they are added. Plasticizers for plastics include phthalates, that give hard plastics like PVC the desired flexibility and durability. In our present investigation, propylene glycol & glycerol dissolved in water disrupts the hydrogen bonding between water molecules such that the mixture cannot form a stable crystal structure unless the temperature is significantly lowered. The present investigation involves the measurements of ultrasonic velocity, density and viscosity in certain binary mixtures. From the measured values, acoustic and thermodynamic parameters were calculated to identify the thermodynamic stability in the mixtures. The excess parameters are computed to study the strength of interactions between the molecules. Theoretical model velocities are also investigated for the binary systems to confirm the type of interaction and to identify the solute – solvent interactions. An attempt has been made to establish that the ultrasonic investigation is a successful technique to identify the specific interactions in certain binary systems [1].

The results have been discussed in terms of molecular interactions. 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 ($ß$), acoustical impedance (Z), molar sound velocity (R), Wada's constant (W), molar volume (V_m), free volume (V_f), intermolecular free length (L_f), internal pressure (π), absorption coefficient (α/f^2) viscous relaxation time (ι), degree of intermolecular attraction (α), excess ultrasonic velocity (U^E), excess adiabatic compressibility ($ß^E$) , excess acoustical impedance (Z^E), excess free length (L_f^E) and excess molar volume (V_m^E) 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.

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 X 10^{-5} m^3 double arm pycnometer. The density values from triplicate replication at the temperature of 303 K were reproducible within ± 2 X 10^{-2} kg m^{-3}. The uncertainty in density and excess molar volume values were found to be ± 4 X 10^{-2} kg m^{-3} and ± 0.001 X 10^{-6} m^3 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 ± 0.005 X 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 (ßs) was calculated by the equation

$$ß = 1/ \rho U^2 \quad (1)$$

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

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

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

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

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

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

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

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

$$L_f = k\, ß^{½} \quad (5)$$

Where K = 1.98 X 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 X 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

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

The viscous relaxation time was calculated by the equation

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

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

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

Where $u^2_{im} = 1/ \{(x_1M_1 + x_2M_2)(x_1/M_1u_1^2 + x_2/M_2u_2^2)\}$

The U^E, $ß^E$, Z^E, L_f^E, and V_m^E were derived over the entire mole fraction range by using the general equation

$$A^E = A - (X_i A_1 + (1\text{-}X_i) A_2) \quad (11)$$

Where A is the corresponding parameters (U, ß, 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

$$U_{IM} = (X_1Z_1 + X_2Z_2) / (X_1\rho_1 + X_2\rho_2) \quad (12)$$

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

$$U_{NR} = [R/V]^3 = \left\{ \frac{(X_1R_1 + X_2R_2)}{(X_1V_1 + X_2V_2)} \right\}^3 \quad (13)$$

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 deal etal. The expression for sound velocity (U_{IMR}) of binary mixtures can be obtained from equation

$$U_{IMR} = \left\{ \frac{[1/(X_1M_1 + X_2M_2)]}{[X_1/M_1U_1^2 + X_2/M_2U_2^2]} \right\}^{1/2} \quad (14)$$

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

$$U_{jun} = \left\{ \frac{(X_1V_1 + X_2V_2)}{(X_1M_1 + X_2M_2)^{1/2}} \left[\frac{X_1V_1}{\rho_1U_1^2} + \frac{X_2V_2}{\rho_2U_2^2} \right] \right\}^{-1/2} \quad (15)$$

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

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

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	η Nsm^{-2}

Zinc stearate	1404	1133	-
Propylene glycol	1624	1030	22.4
Glycerol	1896	1261	1.44

Table 2 gives the measured and acoustic parameters such as ultrasonic velocities (U), density (ρ), viscosity (η), adiabatic compressibility (ß), acoustical impedence (Z), molar sound velocity (R), molar compressibility (W), molar volume (V_m), free volume (V_f), Table 3 gives the thermodynamic properties like intermolecular free length (L_f), internal pressure (π), absorption coefficient (α/f^2), viscous relaxation time (ι), degree of intermolecular attraction (α), Table 4 gives the excess parameters like excess ultrasonic velocity (U^E), excess adiabatic compressibility ($ß^E$) , excess acoustical impedance (Z^E) , excess free length (L_f^E), excess molar volume (V_m^E), 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 - nitrobenzene and calcium stearate - nitrobenzene 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}	η Nsm^{-2}	β / 10^{-10} $Kg^{-1}ms^{-2}$	Z / 10^6 $Kg\,m^{-2}s^{-1}$	R	W	V_m / 10^{-1} m^3mole^{-1}	V_f / 10^{-8} m^3mole^{-1}
zinc stearate – propylene glycol									
0.01	1688	1036.3	27.3	3.39	1.75	0.88	1.66	0.738	0.116
0.02	1760	1042.6	27.7	3.10	1.84	0.89	1.68	0.738	0.122
0.03	1872	1048.9	28.6	2.72	1.96	0.91	1.71	0.737	0.128
0.04	1892	1055.2	28.9	2.65	2.00	0.91	1.72	0.737	0.129
0.05	2016	1061.6	29.7	2.32	2.14	0.93	1.75	0.736	0.138
0.06	2064	1067.9	30.3	2.20	2.20	0.94	1.76	0.736	0.140
0.07	2148	1074.2	30.9	2.02	2.31	0.95	1.78	0.735	0.145
0.08	2184	1080.5	31.6	1.94	2.36	0.95	1.79	0.734	0.145
0.09	2200	1086.8	32.5	1.90	2.39	0.95	1.80	0.734	0.142
0.1	2312	1093.2	32.8	1.71	2.53	0.97	1.82	0.733	0.151
zinc stearate – glycerol									
0.01	1923	1267.3	1.55	2.13	2.44	0.91	1.76	0.730	13.9
0.02	1968	1273.6	1.60	2.03	2.51	0.91	1.77	0.729	13.8
0.03	2084	1279.9	1.67	1.80	2.67	0.93	1.80	0.729	14.2
0.04	1956	1286.2	1.74	2.03	2.52	0.91	1.77	0.728	12.2
0.05	1942	1292.6	1.81	2.05	2.51	0.91	1.76	0.728	11.4
0.06	1964	1298.2	1.88	2.00	2.55	0.91	1.77	0.727	11.0
0.07	2098	1305.2	1.93	1.74	2.74	0.93	1.80	0.727	11.8
0.08	2146	1311.5	2.01	1.66	2.81	0.94	1.81	0.726	11.6
0.09	1980	1317.8	2.12	1.94	2.61	0.91	1.77	0.726	95.0
0.1	2408	1324.2	2.20	1.30	3.19	0.97	1.87	0.725	12.2

Table 3: Thermodynamic parameters of binary mixtures at 303 K

Conc of stearate	L_f / 10^{-11} M	π / 10^6 atm	α/f^2 / 10^{-11} $m^{-1}s^2$	ι / 10^{-09} s	α / 10^{-1} M
zinc stearate – propylene glycol					
0.01	3.65	27.2	14.4	12.3	0.855
0.02	3.49	26.8	12.8	11.5	1.86
0.03	3.27	26.4	10.9	10.4	3.48
0.04	3.23	26.3	10.6	10.2	3.83
0.05	3.02	25.8	8.99	9.19	5.78
0.06	2.94	25.7	8.50	8.89	6.61
0.07	2.82	25.4	7.64	8.32	8.07
0.08	2.76	25.4	7.39	8.18	8.77
0.09	2.74	25.6	7.37	8.23	9.13
0.1	2.60	25.0	6.39	7.49	11.2
zinc stearate – glycerol					
0.01	2.90	5.57	0.451	0.440	0.325
0.02	2.82	5.58	0.432	0.432	0.854

0.03	2.66	5.53	0.378	0.400	2.22
0.04	2.83	5.82	0.475	0.471	0.802
0.05	2.84	5.95	0.503	0.495	0.686
0.06	2.80	6.03	0.503	0.501	0.969
0.07	2.62	5.90	0.422	0.449	2.56
0.08	2.55	5.94	0.407	0.443	3.19
0.09	2.76	6.35	0.546	0.548	1.27
0.1	2.26	5.85	0.313	0.382	6.73

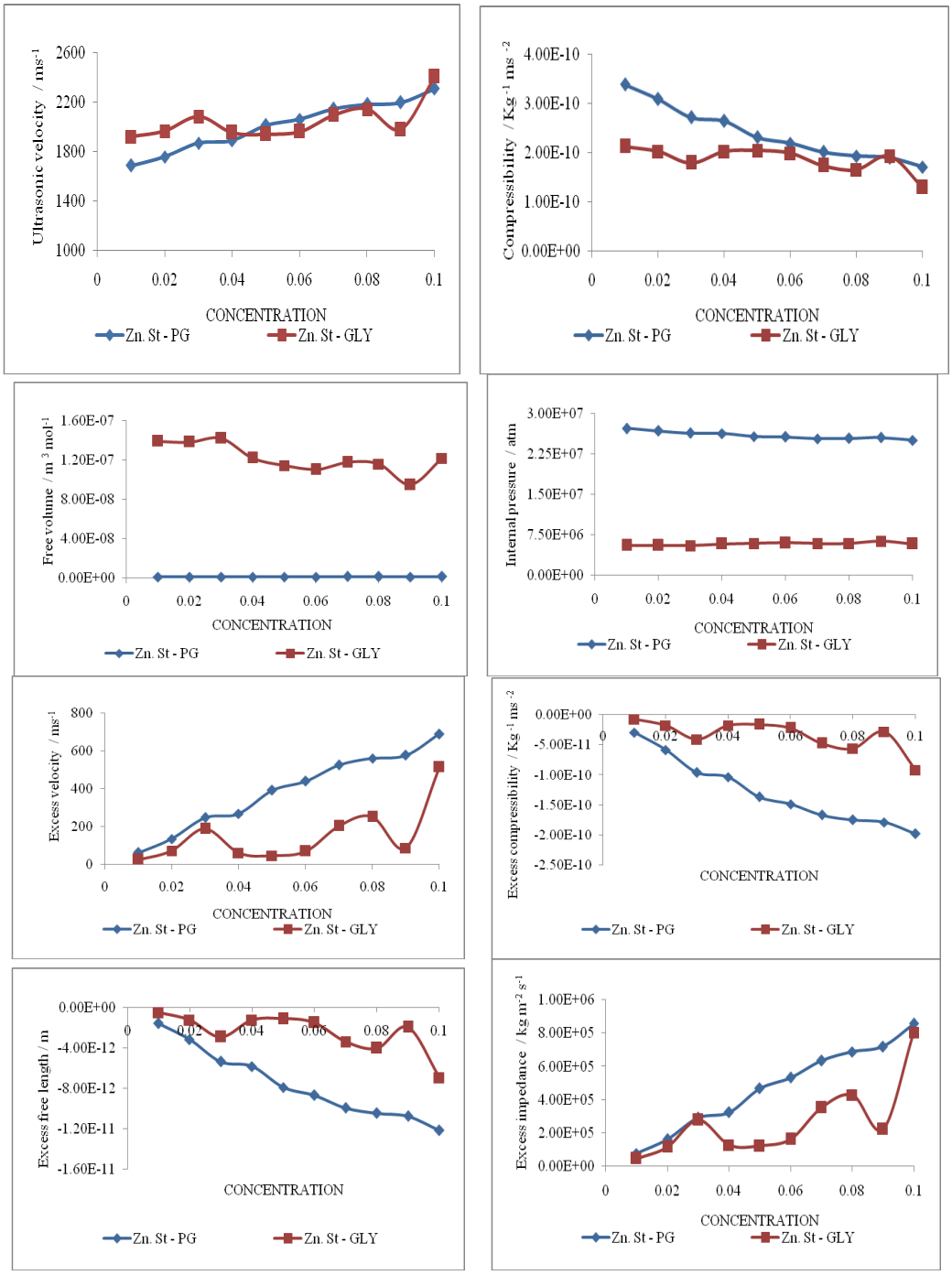
Table 4: Excess parameters of binary mixtures like U^E, $ß^E$, Z^E,L_f^E and v_m^E at 303 K

Conc of stearate	U^E ms^{-1}	β^E / 10^{-11} $Kg^{-1}ms^{-2}$	Z^E / 10^5 $Kg\ m^{-2}s^{-1}$	L_f^E / 10^{-12} m	V_m^E / 10^{-3} m^3mole^{-1}
zinc stearate – propylene glycol					
0.01	64	-2.95	0.766	-1.56	-0.412
0.02	136	-5.86	1.62	-3.16	-0.823
0.03	248	-9.63	2.91	-5.35	-1.23
0.04	269	-10.4	3.24	-5.80	-1.64
0.05	393	-13.7	4.68	-7.88	-2.05
0.06	441	-14.9	5.32	-8.67	-2.46
0.07	525	-16.7	6.35	-9.91	-2.87
0.08	561	-17.5	6.88	-10.5	-3.28
0.09	577	-17.9	7.19	-10.7	-3.68
0.1	690	-19.8	8.55	-12.1	-4.09
zinc stearate – glycerol					
0.01	27	-0.73	0.468	-0.49	-0.407
0.02	73	-1.82	1.17	-1.24	-0.814
0.03	189	-4.12	2.78	-2.89	-1.22
0.04	61	-1.81	1.27	-1.22	-1.62
0.05	48	-1.63	1.22	-1.10	-2.03
0.06	70	-2.20	1.64	-1.49	-2.43
0.07	205	-4.77	3.52	-3.36	-2.84
0.08	253	-5.64	4.28	-4.01	-3.24
0.09	87	-2.85	2.24	-1.95	-3.64
0.1	516	-9.20	8.04	-6.92	-4.04

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}					% Deviation			
	EXPT	Imp	Nom	VDV	Junjie's	Imp	Nom	VDV	Junjie's
zinc stearate – propylene glycol									
0.01	1688	1624	1623	1620	1623	-3.952	-4.023	-4.189	-4.032
0.02	1760	1624	1621	1616	1621	-8.398	-8.544	-8.889	-8.563
0.03	1872	1623	1620	1613	1620	-15.309	-15.541	-16.091	-15.571
0.04	1892	1623	1619	1609	1618	-16.554	-16.865	-17.604	-16.905
0.05	2016	1623	1618	1605	1617	-24.206	-24.618	-25.602	-24.670
0.06	2064	1623	1617	1601	1616	-27.177	-27.680	-28.887	-27.744
0.07	2148	1623	1615	1598	1614	-32.367	-32.975	-34.438	-33.052
0.08	2184	1623	1614	1594	1613	-34.600	-35.302	-37.000	-35.391
0.09	2200	1622	1613	1591	1612	-35.601	-36.392	-38.313	-36.492
0.1	2312	1622	1612	1587	1611	-42.520	-43.439	-45.679	-43.553
zinc stearate – glycerol									
0.01	1923	1896	1893	1892	1891	-1.441	-1.585	-1.614	-1.685
0.02	1968	1895	1890	1889	1886	-3.833	-4.126	-4.185	-4.327
0.03	2084	1895	1887	1885	1882	-9.972	-10.434	-10.529	-10.750
0.04	1956	1895	1884	1882	1877	-3.235	-3.811	-3.930	-4.202
0.05	1942	1894	1881	1879	1873	-2.513	-3.225	-3.375	-3.704
0.06	1964	1894	1879	1875	1868	-3.692	-4.551	-4.735	-5.126
0.07	2098	1894	1876	1872	1864	-10.785	-11.851	-12.082	-12.559
0.08	2146	1893	1873	1869	1860	-13.339	-14.579	-14.851	-15.397
0.09	1980	1893	1870	1865	1855	-4.590	-5.871	-6.155	-6.710
0.1	2408	1893	1868	1862	1851	-27.219	-28.942	-29.330	-30.063

Figure 1: Computed and excess parameters of zinc stearate – PG and zinc stearate – GLY at 303 K



It can be observed from values (Tables 1 - 5 and Fig. 1) that the ultrasonic velocity (U) is found to increase with increase in concentration of stearates. 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 or three hydroxyl groups in glycol or glycerol molecules of plasticizers. Hence, as the sound wave passes, more sound energy has to be utilized to break the large number of intermolecular hydrogen bonds [2]. The molecules of glycol and glycerol may break the structure of stearates and forms intermolecular hydrogen bonds among the components. In Zn. St – PG system, ultrasonic velocity

values increases with increase in stearate concentration. 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.

Stearates are metal soaps that are immiscible in polar solvents such as glycols and glycerol. However, by passing high frequency mechanical waves in binary mixtures, it favours mixing of two components to small extent leading to less interaction. In Zn. St – GLY, systems, ultrasonic velocity values shows non - linear variation predicting the mixture is immiscible blend. The decrease in ultrasonic velocity is due to weakening of molecular interaction [3] and also reveals the absence of disruption of like molecular association by the components on one another and absence of strong dipole – induced dipole interaction between unlike molecules. In addition of stearate to glycols or glycerol, molecular interactions follow the order

Zn. St – PG > Zn. St – GLY

The adiabatic compressibility (β) decreases with increase in stearate concentration for Zn. St – PG system. Comparatively, Zn. St – GLY system shows non linear variation, may be due to the increase in compactness of the system by approach of unlike molecules [4]. The change in adiabatic compressibility indicates that there is definite contraction on mixing. Acoustic impedance (Z) increases linearly in Zn. St – PG systems, confirms the presence of molecular association between stearate - glycol molecules through intermolecular hydrogen bonding [5]. However non linear variation in Zn. St – GLY systems indicates the formation of cluster in solution. Molar volume (V_m) decreases with increase in stearate concentration and it varies based on the addition of glycols and glycerol, it follows the order propylene glycol > glycerol

The variation of free volume (V_f) shows non linear variation with increase and decrease values of V_f with increase in stearate concentration for Zn. St – PG. The reverse trend of non linear variation is observed in Zn. St – GLY systems. The intermolecular free length (L_f) also follows the same trend as that of adiabatic compressibility. For Zn. St – PG system, 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 and also decrease with increase in the chain length of the glycols. For Zn. St – GLY system, free length decrease and increase with increase in stearate concentration which confirms the presence of weak interaction. It can be seen from the data, it suggests that the internal pressure (π_i) Zn. St – PG system, internal pressure decrease at low concentration but as stearate concentration increases, internal pressure increases predicting strong interaction is possible among the components in binary mixture. Further Zn. St – GLY system follows the reverse trend indicating weak interaction at high stearate concentration. 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 exist between unlike components and decreased values explains that the interaction occurs between like components [5]. α value increase for Zn. St – PG system, identifies the existence of interaction among them. Increase in number of carbon atoms among the component increases interaction parameter values. In Zn. St – GLY, system, α value increases at low stearate concentration identifying the presence of molecular interaction. Comparatively, it decreases at higher stearate concentration revealing the absence of complex formation.

The excess velocity (U^E) shows positive deviations [6] predicts the presence of weak interaction which may be due to dispersion force. It shows non linear variation for Zn. St – PG and Zn. St – GLY systems. It states that molecular association of the component is stronger than dissociation of the molecules. Increase in compactness between the molecules leading to solute – solvent interaction. This is confirmed by greater negative deviation in Zn. St – PG system. Comparatively binary mixtures Zn. St – GLY systems shows less negative deviation [7] implies that the specific interaction may be due to structure breaking effect which dominates the dispersive interaction between unlike molecules. It was reported that the positive deviation in excess impedance (Z^E) indicates the presence of strong interactions between component molecules in the binary mixtures [8]. Binary mixtures Zn. St – PG & Zn. St – GLY shows non linear variation which identifies strong molecular interaction among them.

The experimental and theoretical velocities calculated by using various empirical relations are presented [9]. 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. For Zn. St – PG system, deviation follows the order $U_{Vdv} > U_{Jun} > U_{Nom} > U_{Imp}$ and for Zn. St – GLY systems, deviation follows as $U_{Jun} > U_{Vdv} > U_{Nom} > U_{Imp}$.

Conclusion:

The present investigation measures ultrasonic velocity, density and viscosity of stabilizers with plasticizers at 303 K [10]. 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. In both Zn. St – PG & Zn. St – GLY systems shows only weak physical attraction indicating that the mixture is immiscible blend which may be due to the increase in chain length and decrease in strength of association.

Zn. St – PG > Zn. St – GLY

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