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THE MOLECULAR INTERACTION STUDY OF CALCIUM STEARATE WITH PROPYLENE GLYCOL AND GLYCEROL

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Abstract:

We report the measurements of ultrasonic velocity in the binary mixtures of calcium stearate – propylene glycol and calcium 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:

The use of plastic is growing exponentially every year and most of the synthetic plastics are not biodegradable and hence they are not eco - friendly. There is a need for the discovery of biodegradable polymers and hence extensive research is going on to make the synthetic plastics biodegradable under suitable conditions. Plastics are usually stabilized by the addition of certain compounds (stabilizers). Solvents like acetone, methyl ethyl ketone and plasticizers like phthalates, glycols and glycerol are used in the processing of these polymers. Extensive studies on molecular interaction between polymers, solvents, stabilizers and plasticizers would be useful in making the plastics biodegradable as some microbes have the tendency to interact with these components and accelerate biodegradation. Ultrasonic study has been used as a non - destructive technique for molecular interaction studies. In our present investigation, Calcium stearate is used as stabilizer in manufacture of biodegradable plastics. Plasticizers are additives that increase the flexibility and durability. In our present investigation, propylene glycol & glycerol are mixed with calcium stearate and its molecular interaction in binary mixture is studied.

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

$$ß = 1/\rho U^2 \qquad (1)$$

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

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

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

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

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

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

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

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

$$L_f = k\, ß^{½} \qquad (5)$$

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

The Free volume was calculated by the equation

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

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

The internal pressure was calculated by the equation

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

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

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

The viscous relaxation time was calculated by the equation

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

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

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

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

$$A^E = A - (X_i A_1 + (1-X_i) A_2) \qquad (11)$$

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

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

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

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

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

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

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

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

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

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

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/m³	η Nsm⁻²
Calcium stearate	1310	1145	-

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}
calcium stearate – propylene glycol									
0.01	1694	1036.0	29.1	3.36	1.76	0.88	1.67	0.738	0.106
0.02	1780	1042.1	29.3	3.03	1.85	0.89	1.69	0.738	0.114
0.03	2032	1048.2	29.6	2.31	2.13	0.93	1.75	0.737	0.138
0.04	2056	1054.3	30.0	2.24	2.17	0.94	1.76	0.737	0.139
0.05	2224	1060.3	30.3	1.91	2.36	0.96	1.80	0.736	0.155
0.06	2284	1066.4	30.7	1.80	2.44	0.97	1.81	0.736	0.159
0.07	2292	1072.5	31.2	1.77	2.46	0.97	1.82	0.735	0.157
0.08	2296	1078.6	31.6	1.76	2.48	0.97	1.82	0.734	0.156
0.09	2387	1084.6	31.9	1.62	2.59	0.98	1.84	0.734	0.165
0.1	2393	1090.7	32.2	1.60	2.61	0.98	1.84	0.733	0.164
calcium stearate – glycerol									
0.01	1940	1267.0	1.65	2.10	2.46	0.91	1.76	0.730	12.8
0.02	2108	1273.1	1.70	1.77	2.68	0.94	1.80	0.729	14.0
0.03	1956	1279.2	1.79	2.04	2.50	0.91	1.77	0.729	11.6
0.04	1985	1285.2	1.80	1.97	2.55	0.92	1.77	0.728	11.4
0.05	2082	1291.3	1.93	1.79	2.69	0.93	1.80	0.728	11.5
0.06	2145	1297.4	1.99	1.68	2.78	0.94	1.81	0.727	11.6
0.07	2378	1303.4	2.08	1.36	3.10	0.97	1.87	0.727	12.7
0.08	1945	1309.5	2.17	2.02	2.55	0.91	1.76	0.726	8.86
0.09	2420	1315.6	2.23	1.30	3.18	0.97	1.88	0.726	11.9
0.1	2252	1321.6	2.32	1.49	2.98	0.95	1.84	0.725	10.1

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
calcium stearate – propylene glycol					
0.01	3.64	28.1	15.2	13.0	0.930
0.02	3.45	27.4	13.1	11.8	2.12
0.03	3.02	25.7	8.85	9.12	5.87
0.04	2.97	25.7	8.60	8.96	6.32
0.05	2.74	24.8	6.83	7.71	9.18
0.06	2.66	24.6	6.36	7.36	10.3
0.07	2.64	24.7	6.35	7.38	10.5
0.08	2.63	24.8	6.36	7.40	10.7
0.09	2.52	24.3	5.68	6.87	12.5
0.1	2.51	24.4	5.66	6.87	12.7
calcium stearate – glycerol					
0.01	2.87	5.73	0.469	0.461	0.507
0.02	2.64	5.57	0.375	0.401	2.45
0.03	2.84	5.92	0.492	0.488	0.757

0.04	2.79	5.95	0.482	0.485	1.12
0.05	2.65	5.95	0.436	0.461	2.27
0.06	2.57	5.93	0.408	0.444	3.07
0.07	2.31	5.75	0.312	0.376	6.12
0.08	2.82	6.49	0.593	0.585	0.822
0.09	2.26	5.88	0.314	0.386	6.81
0.1	2.42	6.22	0.405	0.462	4.61

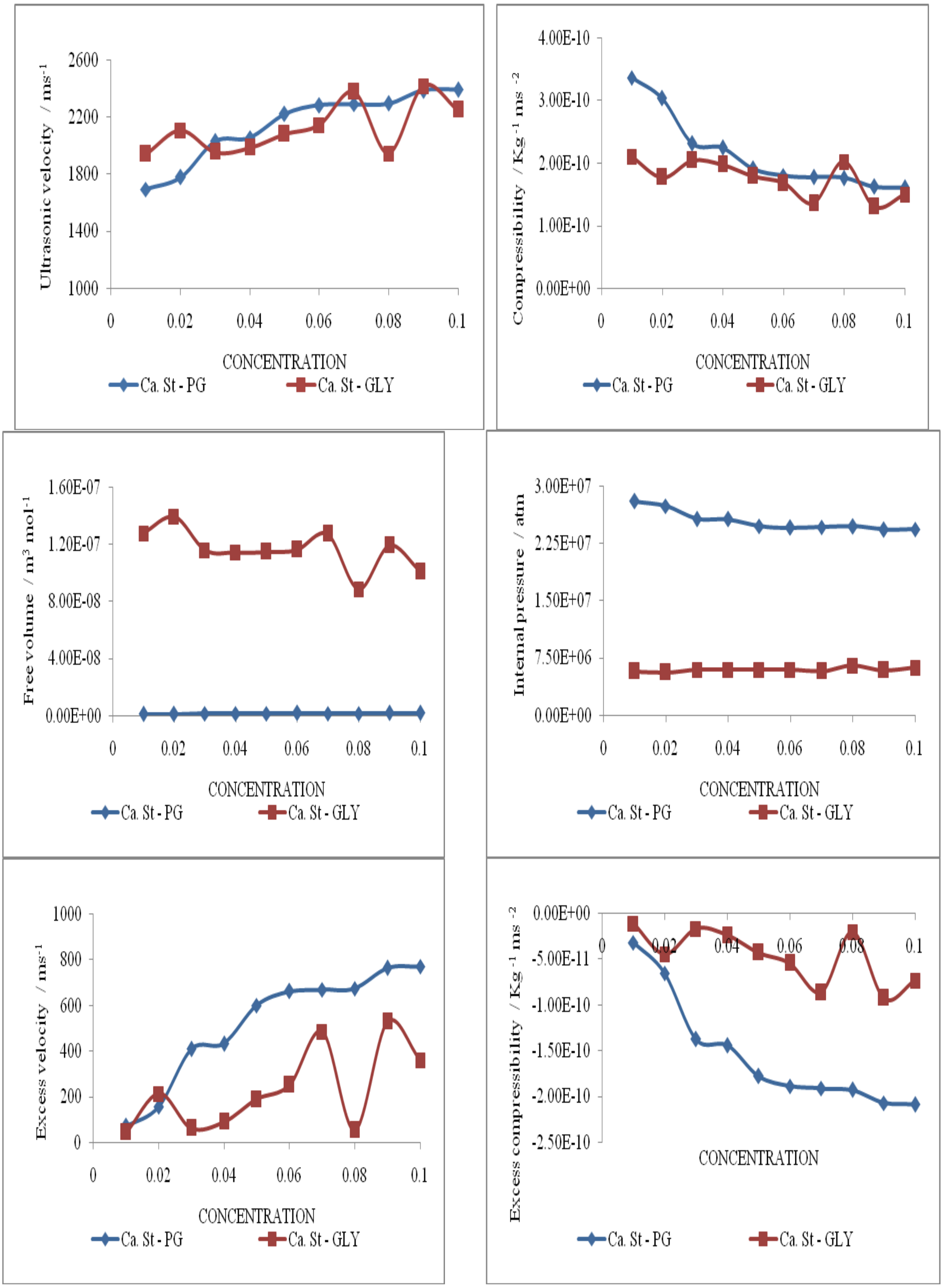
Table 4: Excess parameters of binary mixtures like U^E, $ß^E$, Z^E,L_f^E and v_m^E at 303 K

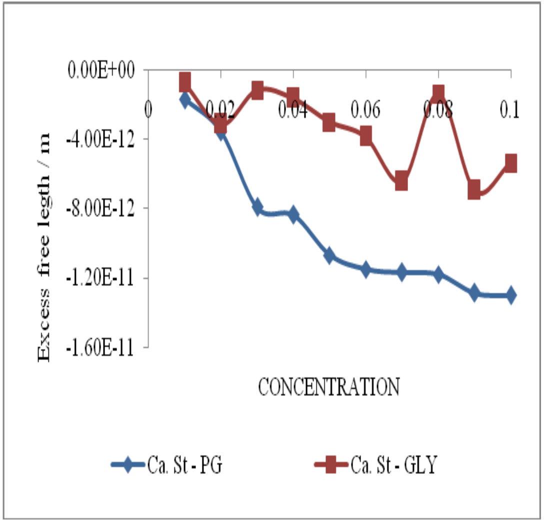
Conc of stearate	U^E ms^{-1}	$β^E$ / 10^{-10} $Kg^{-1}ms^{-2}$	Z^E / 10^5 Kg $m^{-2}s^{-1}$	L_f^E / 10^{-12} m	V_m^E / 10^{-3} m^3mole^{-1}
calcium stearate – propylene glycol					
0.01	70	-3.19	0.825	-1.68	-0.389
0.02	156	-6.55	1.83	-3.55	-0.781
0.03	409	-13.7	4.58	-7.92	-1.17
0.04	433	-14.4	4.95	-8.37	-1.56
0.05	601	-17.8	6.86	-10.7	-1.95
0.06	661	-18.9	7.64	-11.5	-2.34
0.07	670	-19.1	7.86	-11.7	-2.73
0.08	674	-19.3	8.05	-11.8	-3.12
0.09	765	-20.7	9.17	-12.9	-3.50
0.1	771	-20.9	9.39	-13.0	-3.89
calcium stearate – glycerol					
0.01	44	-1.11	0.678	-0.748	-0.385
0.02	213	-4.43	2.94	-3.11	-0.772
0.03	61	-1.69	1.13	-1.14	-1.16
0.04	91	-2.40	1.63	-1.63	-1.54
0.05	188	-4.30	3.01	-3.01	-1.93
0.06	252	-5.43	3.96	-3.86	-2.31
0.07	485	-8.64	7.13	-6.44	-2.70
0.08	52	-2.04	1.61	-1.37	-3.08
0.09	528	-9.27	7.99	-6.96	-3.46
0.1	360	-7.35	5.92	-5.35	-3.84

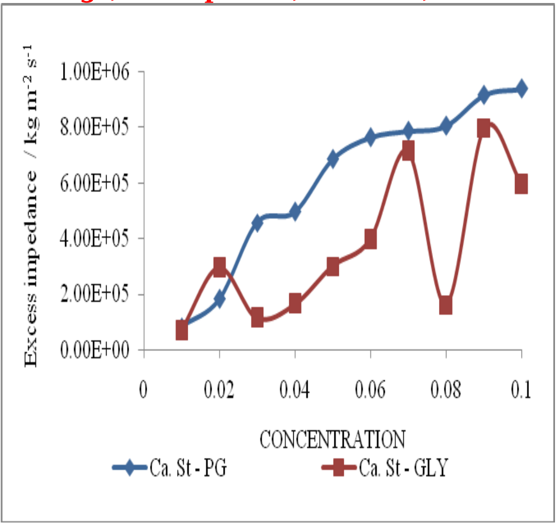
Table 5: Experimental velocities and theoretical velocities along with the percentage deviation of binary mixtures at 303 K

Conc of stearate	Ultrasonic velocity U / ms^{-1}					% Deviation			
	EXPT	Imp	Nom	VDV	Junjie's	Imp	Nom	VDV	Junjie's
calcium stearate – propylene glycol									
0.01	1694	1624	1622	1620	1622	-4.327	-4.424	-4.546	-4.446
0.02	1780	1623	1620	1617	1620	-9.641	-9.844	-10.102	-9.889
0.03	2032	1623	1619	1613	1618	-25.183	-25.530	-25.972	-25.607
0.04	2056	1623	1617	1609	1616	-26.681	-27.148	-27.743	-27.250
0.05	2224	1623	1615	1606	1614	-37.054	-37.681	-38.485	-37.818
0.06	2284	1622	1614	1602	1612	-40.774	-41.543	-42.533	-41.710
0.07	2292	1622	1612	1599	1610	-41.289	-42.185	-43.345	-42.379
0.08	2296	1622	1610	1595	1608	-41.558	-42.579	-43.905	-42.798
0.09	2387	1622	1609	1592	1606	-47.191	-48.379	-49.928	-48.633
0.1	2393	1621	1607	1589	1604	-47.585	-48.901	-50.626	-49.181
calcium stearate – glycerol									
0.01	1940	1896	1893	1893	1890	-2.342	-2.508	-2.503	-2.646
0.02	2108	1895	1889	1889	1884	-11.227	-11.588	-11.578	-11.886
0.03	1956	1895	1886	1886	1878	-3.228	-3.728	-3.715	-4.139
0.04	1985	1894	1882	1883	1873	-4.780	-5.454	-5.438	-6.004
0.05	2082	1894	1879	1879	1867	-9.922	-10.801	-10.783	-11.513
0.06	2145	1894	1876	1876	1862	-13.272	-14.354	-14.333	-15.225
0.07	2378	1893	1873	1873	1856	-25.601	-26.996	-26.972	-28.109
0.08	1945	1893	1869	1870	1851	-2.752	-4.050	-4.030	-5.079
0.09	2420	1893	1866	1866	1846	-27.871	-29.679	-29.655	-31.103
0.1	2252	1892	1863	1863	1841	-19.019	-20.880	-20.859	-22.336

Figure 1" Computed and excess parameters of calcium stearate – PG and calcium stearate – GLY at 303 K







The increase in ultrasonic velocity (Tables 1 - 5 and Fig. 1) 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 gradual increase of sound absorption with glycol and glycerol concentration strongly supports the intermolecular association through hydrogen bonding between the solute and solvent molecules. This may be explained as follows, as concentration of plasticizer increase, hydroxyl group in glycol and glycerol increases. Consequently stronger viscous forces are predominantly present between solute – solvent and solvent – solvent molecules.

In Ca. St – PG system, It identifies the presence of solute - solvent type of interaction between the contributing molecules [1]. 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. Ultrasonic velocity increases as the number of carbon atoms increases in the molecule and due to the presence of long chain and ring structured components. In Ca. St – GLY, systems, U shows non - linear variation predicting the mixture is immiscible blend [2]. As molecular interaction decreases, ultrasonic velocity also decreases [9] and also reveals the absence of disruption of like molecular association by the components on one another In addition of stearate to glycols or glycerol, molecular interactions follow the order
Ca. St – PG > Ca. St – GLY

The adiabatic compressibility (β) decreases with increase in stearate concentration for Ca. St – PG system. Comparatively, Ca. St – GLY system shows non linear variation, may be due to the increase in compactness of the system by approach of unlike molecules. The change in adiabatic compressibility indicates that there is definite contraction on mixing [3]. 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. Increase in chain length of the component decreases adiabatic compressibility which reveals the intermolecular interactions leading to compact structural arrangement. Acoustic impedance (Z) increases linearly in Ca. St – PG systems, confirms the presence of molecular association between stearate - glycol molecules through intermolecular hydrogen bonding. However non linear variation in Ca. St – GLY systems indicates the formation of cluster in solution [4]. 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 both Ca. St – PG & Ca. St – GLY systems. For Ca. 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 [5]. For Ca. St – GLY system, weak interaction is observed from non linear trend values. For both Ca. St – PG, Ca. St – GLY 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 [6]. For Ca. St – PG system, the existence of molecular interaction occurs among them. Increase in number of carbon atoms among the component increases interaction parameter values. For Ca. St – GLY systems, α value increases at low stearate concentration. Comparatively, it decreases at higher stearate concentration. For both Ca. St – PG and Ca. St – GLY systems, U^E shows positive deviations [7] predicts non linear variation, that favours molecular association between the mixtures

Chemical interaction leads to negative values of both excess compressibility values (β^E) and free length (L_f^E) [8]. It also reveals the presence of interstitial accommodation between the components in Ca. St – PG systems. Comparatively, for Ca. St – GLY system, it indicates the existence of less molecular interaction between stabilizers and plasticizers [9]. Excess impedance increases with increase in stearate concentration confirms the strong molecular interaction. Binary mixtures Ca. St – PG & Ca. 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. Negative deviation is observed for all the 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. For Ca. St – PG system, deviation follows the order $U_{Vdv} > U_{Jun} > U_{Nom} > U_{Imp}$ and for Ca. St – GLY system, deviation follows as $U_{Jun} > U_{Nom} > U_{Vdv} > U_{Imp}$.

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 Ca. St – PG system, maximum molecular interaction is observed. It predicts the disruption of like forces in glycols and association of both components occurs partially. However, Ca. St – GLY system there is a possibility of interstitial accommodation due to the different sizes of the solute and solvent molecules.

Ca. St – PG > Ca. St – GLY

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