

Molecular Interaction Studies with Zinc Stearate, Calcium Stearate and Ethylene Glycol

C. Ravichandran¹, R. Kavitha¹, S. Jayakumar², R. Anusa¹

Department of Chemistry, Easwari Engineering College, Chennai, India¹

Department of Physics, Vivekananda College, Mylapore, Chennai, India²

ABSTRACT: Industry demands reliable and accessible reference data on the physical and chemical properties of a wide variety of binary mixtures. These data are required in the development of models for process design, energy efficiency and in the evaluation of possible environmental impacts. 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. Speed of sound have been measured as a function of composition for binary mixtures of stearates (zinc stearate and calcium stearate) and ethylene 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 – ethylene glycol and calcium stearate – ethylene 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 usefulness of assessment in self – association of stabilizers and plasticizers is studied. In the present investigations, studies are made with two structurally different stabilizers such as zinc stearate, calcium stearate and plasticizer ethylene glycol. Glycol is generally accepted as compound having two hydroxyl groups attached to different carbon atoms in an aliphatic carbon chain. Glycol finds widespread application in automotive, aviation, explosive, textile, surface coating, food, cosmetic, pharmaceutical, tobacco, petroleum, and other industries. Glycol is 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. Most of the salts are well soluble in water are soluble in glycol too. Glycol is important precursor to polymers, it will break down within several days to a few weeks in presence of air, water and soil. 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. 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 (β), 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 (τ), degree of intermolecular attraction (α), excess ultrasonic velocity (U^E), excess adiabatic compressibility (β^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.

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 $1 \times 10^{-5} \text{ m}^3$ double arm pycnometer. The density values from triplicate replication at the temperature of 303 K were reproducible within $\pm 2 \times 10^{-2} \text{ kg m}^{-3}$. The uncertainty in density and excess molar volume values were found to be $\pm 4 \times 10^{-2} \text{ kg m}^{-3}$ and $\pm 0.001 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ 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 $\approx 0.8738 \text{ g cm}^{-3}$) and doubly distilled water (density $\approx 0.9970 \text{ g cm}^{-3}$) at 303 K. The flow time of pure liquids and liquid mixtures were repeated for five times. The uncertainty of viscosity was $\pm 0.005 \times 10^{-3} \text{ m Pas}$. 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 0.1 ms^{-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

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

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

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

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

International Journal of Innovative Research in Science, Engineering and Technology

An ISO 3297: 2007 Certified Organization

Volume 4, Special Issue 1, February 2015

THIRD NATIONAL CONFERENCE ON ADVANCES IN CHEMISTRY (NCAC – 2015)

On 18th February 2015

Organized by

Department of Chemistry, Easwari Engineering College (SRM Group of Institutions), Chennai-600089, India.

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

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

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

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

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

$$U_{IM} = (X_1 Z_1 + X_2 Z_2) / (X_1 \rho_1 + X_2 \rho_2) \quad (12)$$

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

$$U_{NR} = [R/V]^3 = \left\{ \frac{(X_1 R_1 + X_2 R_2)}{(X_1 V_1 + X_2 V_2)} \right\}^3 \quad (13)$$

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

$$U_{IMR} = \left\{ \frac{[1/(X_1 M_1 + X_2 M_2)]^{1/2}}{[X_1 / M_1 U_1^2 + X_2 / M_2 U_2^2]} \right\} \quad (14)$$

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

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

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

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

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	η Nsm ⁻²
Zinc stearate	1404	1133	-
Calcium stearate	1310	1145	-
Ethylene glycol	1638	960	1.38

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 (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 (τ), degree of intermolecular attraction (α), Table 4 gives the excess parameters like excess ultrasonic velocity (U^E), excess adiabatic compressibility (β^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 - ethylene glycol and calcium stearate – ethylene 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	η / Nsm ⁻²	$\beta / 10^{-10}$ Kg ⁻¹ ms ⁻²	Z / 10 ⁶ Kg m ⁻² s ⁻¹	R	W	$V_m / 10^{-1}$ m ³ mole ⁻¹	$V_f / 10^{-8}$ m ³ mole ⁻¹
zinc stearate – ethylene glycol									
0.01	1708	966.32	1.45	3.55	1.65	0.95	1.77	0.792	9.69
0.02	1728	972.64	1.47	3.44	1.68	0.95	1.78	0.791	9.69
0.03	1748	978.96	1.50	3.34	1.71	0.95	1.79	0.791	9.69
0.04	1752	985.28	1.54	3.31	1.73	0.95	1.79	0.790	9.41
0.05	1760	991.6	1.58	3.26	1.75	0.95	1.79	0.790	9.18
0.06	1764	997.92	1.64	3.22	1.76	0.95	1.79	0.789	8.79
0.07	1768	1004.24	1.70	3.19	1.78	0.95	1.79	0.788	8.43
0.08	1772	1010.56	1.84	3.15	1.79	0.95	1.79	0.788	7.56
0.09	1774	1016.88	1.95	3.12	1.80	0.95	1.79	0.787	7.00
0.1	1782	1023.2	2.08	3.08	1.82	0.95	1.80	0.786	6.45
calcium stearate – ethylene glycol									
0.01	1716	966.04	1.48	3.52	1.66	0.95	1.78	0.792	9.45
0.02	2000	972.12	1.50	2.57	1.94	1.00	1.86	0.791	11.7
0.03	2144	978.2	1.53	2.22	2.10	1.02	1.89	0.791	12.8
0.04	2232	984.28	1.55	2.04	2.20	1.03	1.91	0.790	13.3
0.05	2324	990.32	1.60	1.87	2.30	1.05	1.94	0.790	13.7
0.06	2428	996.4	1.65	1.70	2.42	1.06	1.96	0.789	14.0
0.07	2436	1002.48	1.76	1.68	2.44	1.06	1.96	0.788	12.9
0.08	2448	1008.56	1.90	1.65	2.47	1.06	1.97	0.788	11.7
0.09	2520	1014.6	1.97	1.55	2.56	1.07	1.98	0.787	11.7
0.1	2568	1020.68	2.06	1.49	2.62	1.08	1.99	0.786	11.3

Table 3 : Thermodynamic parameters of binary mixtures at 303 K

Conc of stearate	$L_f / 10^{-11}$ m	$\pi / 10^6$ atm	$\alpha/f^2 / 10^{-11}$ $m^{-1}s^2$	$\tau / 10^{-9}$ s	$\alpha / 10^{-1}$ m
<u>zinc stearate – ethylene glycol</u>					
0.01	3.74	5.95	0.790	0.685	0.929
0.02	3.68	5.95	0.772	0.676	1.24
0.03	3.63	5.95	0.753	0.668	1.56
0.04	3.61	6.01	0.764	0.679	1.67
0.05	3.58	6.07	0.770	0.687	1.84
0.06	3.56	6.16	0.788	0.705	1.95
0.07	3.54	6.25	0.806	0.722	2.06
0.08	3.52	6.48	0.862	0.774	2.18
0.09	3.51	6.66	0.905	0.814	2.26
0.1	3.48	6.84	0.946	0.855	2.43
<u>calcium stearate – ethylene glycol</u>					
0.01	3.72	6.00	0.796	0.693	1.03
0.02	3.18	5.59	0.508	0.516	5.05
0.03	2.96	5.43	0.417	0.453	7.38
0.04	2.83	5.36	0.373	0.423	8.93
0.05	2.71	5.31	0.338	0.398	10.6
0.06	2.59	5.28	0.305	0.376	12.6
0.07	2.57	5.42	0.320	0.395	12.9
0.08	2.55	5.61	0.338	0.420	13.2
0.09	2.47	5.61	0.318	0.407	14.7
0.1	2.42	5.68	0.313	0.408	15.8

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

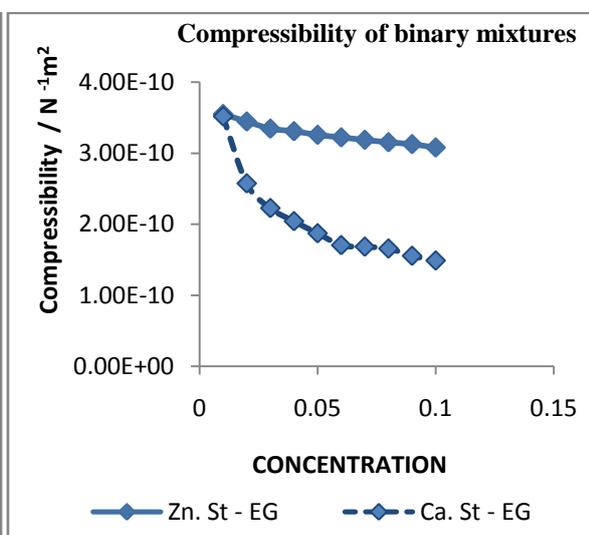
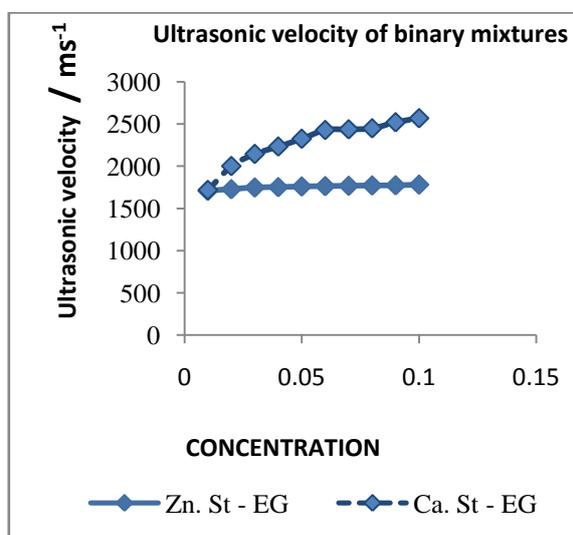
Conc of stearate	U^E ms^{-1}	$\beta^E / 10^{-11}$ $Kg^{-1}ms^{-2}$	$Z^E / 10^5$ $Kg m^{-2}s^{-1}$	$L_f^E / 10^{-12}$ m	$V_m^E / 10^{-3}$ $m^3 mole^{-1}$
<u>zinc stearate – ethylene glycol</u>					
0.01	70	-3.36	0.780	-1.73	-0.442
0.02	90	-4.40	1.08	-2.28	-0.883
0.03	111	-5.41	1.39	-2.82	-1.32
0.04	115	-5.78	1.54	-3.02	-1.76
0.05	123	-6.29	1.73	-3.31	-2.20
0.06	127	-6.65	1.88	-3.50	-2.64
0.07	131	-7.00	2.03	-3.70	-3.08
0.08	135	-7.35	2.18	-3.89	-3.52
0.09	138	-7.62	2.31	-4.04	-3.95
0.1	146	-8.09	2.51	-4.31	-4.39
<u>calcium stearate – ethylene glycol</u>					
0.01	78	-3.68	0.853	-1.90	-0.418
0.02	363	-13.1	3.72	-7.29	-0.838
0.03	507	-16.6	5.25	-9.52	-1.26
0.04	595	-18.5	6.25	-10.8	-1.68
0.05	687	-20.2	7.29	-12.0	-2.09
0.06	792	-21.9	8.47	-13.2	-2.51
0.07	800	-22.1	8.70	-13.4	-2.92
0.08	812	-22.4	8.97	-13.6	-3.34
0.09	884	-23.4	9.85	-14.4	-3.75
0.1	933	-24.1	10.5	-15.0	-4.17

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 – ethylene glycol										
0.01	1708	1638	1637	1634	1636	-4.287	-4.360	-4.540	-4.370	
0.02	1728	1638	1635	1630	1635	-5.523	-5.670	-6.033	-5.689	
0.03	1748	1637	1634	1626	1634	-6.758	-6.980	-7.530	-7.008	
0.04	1752	1637	1633	1622	1632	-7.017	-7.311	-8.045	-7.349	
0.05	1760	1637	1631	1618	1631	-7.520	-7.887	-8.807	-7.934	
0.06	1764	1637	1630	1614	1629	-7.778	-8.218	-9.322	-8.274	
0.07	1768	1636	1629	1610	1628	-8.037	-8.548	-9.837	-8.613	
0.08	1772	1636	1628	1606	1626	-8.296	-8.878	-10.351	-8.951	
0.09	1774	1636	1626	1602	1625	-8.432	-9.084	-10.741	-9.166	
0.1	1782	1636	1625	1598	1624	-8.935	-9.659	-11.505	-9.750	
calcium stearate – ethylene glycol										
0.01	1716	1638	1636	1634	1636	-4.782	-4.880	-5.016	-4.900	
0.02	2000	1637	1634	1630	1634	-22.146	-22.376	-22.693	-22.422	
0.03	2144	1637	1632	1626	1632	-30.965	-31.333	-31.844	-31.407	
0.04	2232	1637	1631	1622	1629	-36.367	-36.875	-37.583	-36.976	
0.05	2324	1636	1629	1618	1627	-42.014	-42.671	-43.591	-42.802	
0.06	2428	1636	1627	1615	1625	-48.397	-49.217	-50.369	-49.379	
0.07	2436	1636	1625	1611	1623	-48.914	-49.869	-51.216	-50.057	
0.08	2448	1636	1624	1607	1621	-49.676	-50.768	-52.313	-50.981	
0.09	2520	1635	1622	1604	1619	-54.106	-55.364	-57.151	-55.609	
0.1	2568	1635	1620	1600	1618	-57.071	-58.488	-60.509	-58.762	



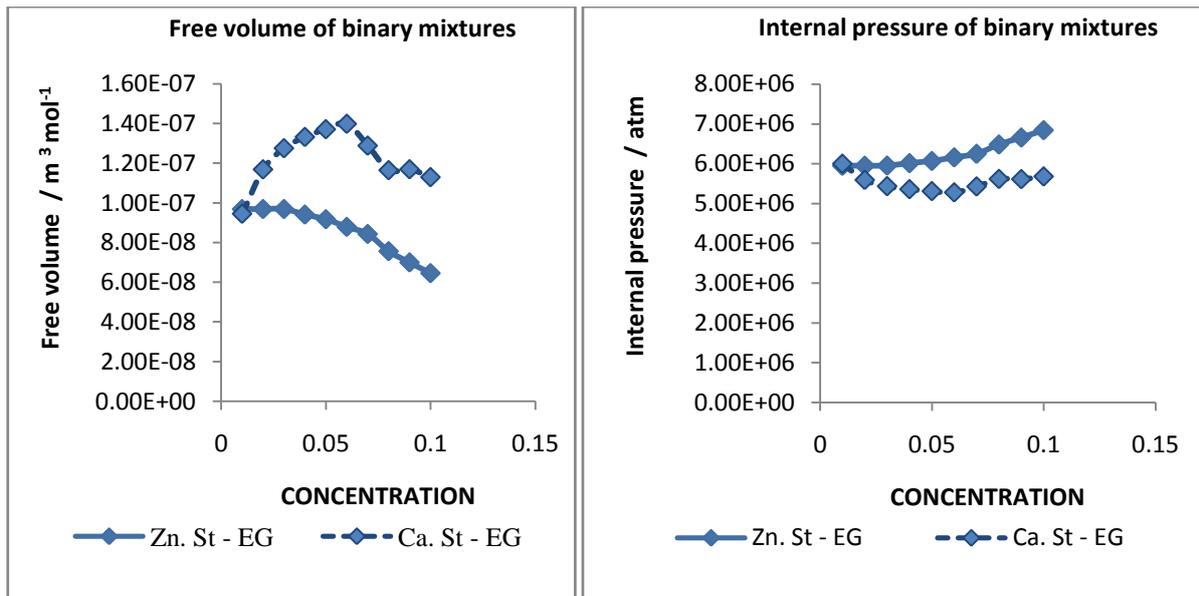
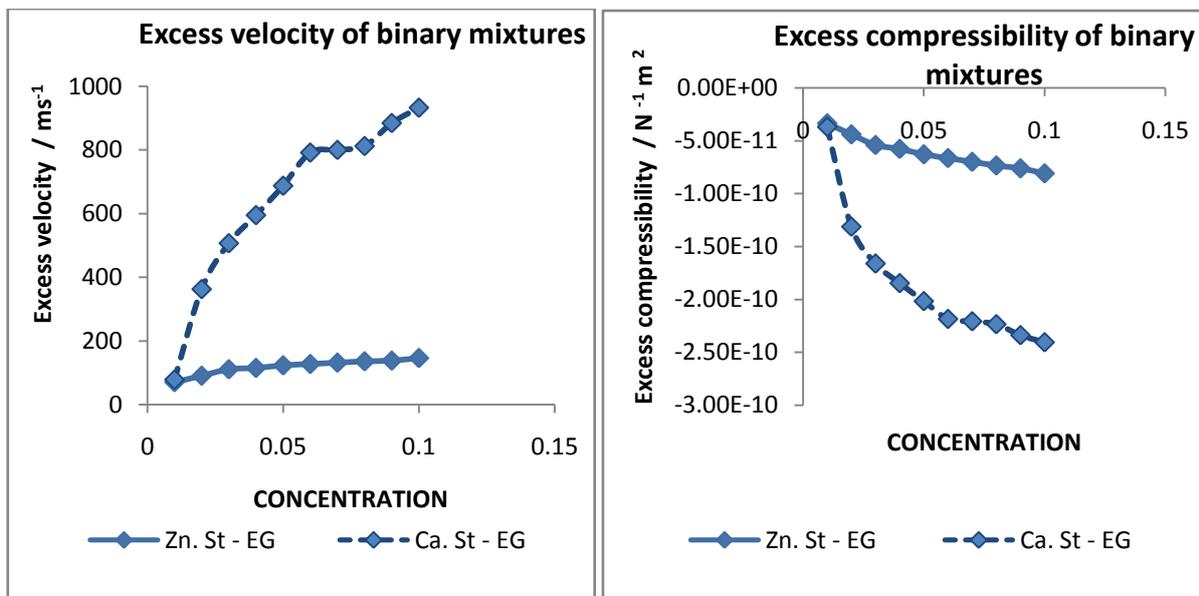


Fig.1 : Computed parameters of zinc stearate – ethylene glycol and calcium stearate – ethylene glycol



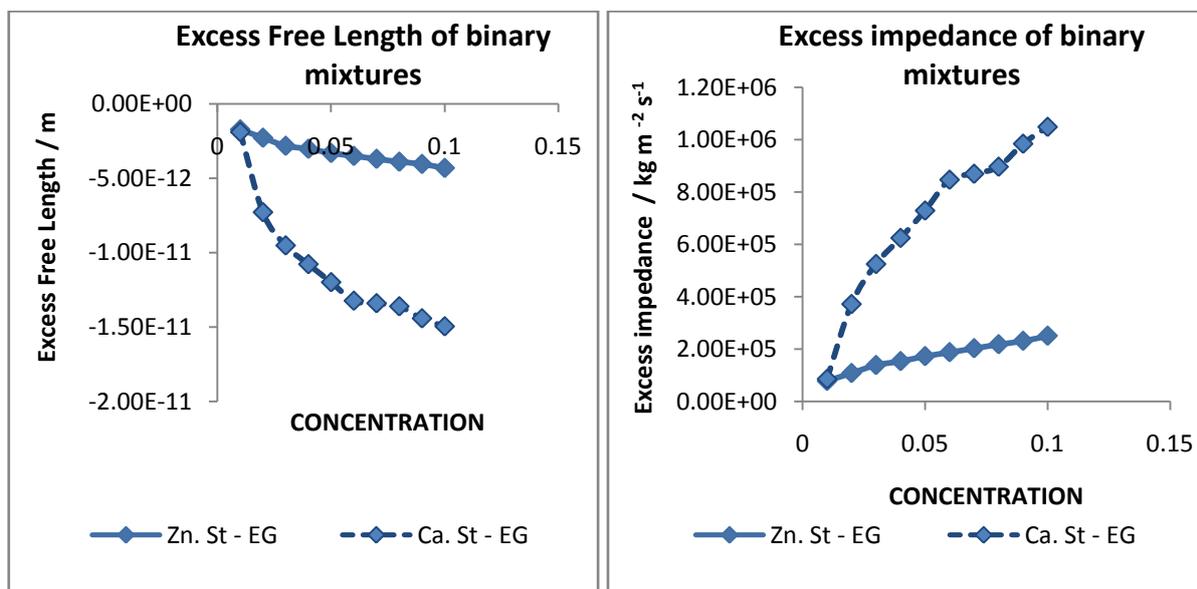


Fig.2 : Excess parameters of zinc stearate – ethylene glycol and calcium stearate – ethylene glycol

It can be observed that the ultrasonic velocity (U) is found to increase with increase in stearate concentration for both the Zn. St – EG and Ca. St – EG systems. 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 plasticizers. The gradual increase of sound absorption with glycol 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 increases. Hence, as the sound wave passes, more sound energy has to be utilized to break the large number of intermolecular hydrogen bonds [4]. The molecules of glycol may break the structure of stearates and forms intermolecular hydrogen bonds among the components. Consequently stronger viscous forces are predominantly present between solute – solvent and solvent – solvent molecules. 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 [5]. 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. The density values (ρ) and viscosity values (η) increases with increase in stearate concentration in both the binary mixtures which predicts that there is greater interaction between the components [6].

The adiabatic compressibility (β) decreases with increase in stearate concentration for Zn. St – EG and Ca. St – EG systems. 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 the systems, confirms the presence of molecular association between stearate - glycol molecules through intermolecular hydrogen bonding [7]. Rao's constant (R) and Wada's constant (W) is constant for binary mixture Zn. St – EG system, predicting the absence of complex formation and shows linear variation for the binary mixtures Ca. St – EG system, revealing the presence of strong interaction than with Zn. St – EG system. Molar volume (V_m) decreases with increase in stearate concentration and it varies based on

International Journal of Innovative Research in Science, Engineering and Technology

An ISO 3297: 2007 Certified Organization

Volume 4, Special Issue 1, February 2015

THIRD NATIONAL CONFERENCE ON ADVANCES IN CHEMISTRY (NCAC – 2015)On 18th February 2015

Organized by

Department of Chemistry, Easwari Engineering College (SRM Group of Institutions), Chennai-600089, India.

the addition of glycol to either zinc stearate or calcium stearate. The variation of free volume (V_f) decreases with increase in stearate concentration for Zn. St – EG system. Free volume decreases due to splitting of a major component and polarization of existing molecule, leads to close packing of molecules with increase in strength of interactions [8]. It shows non linear variation with increase and decrease values of V_f with increase in stearate concentration for Ca. St – EG systems.

The intermolecular free length (L_f) also follows the same trend as that of adiabatic compressibility. For Zn. St – EG and Ca. St – EG 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 [9]. It can be seen from the data that the internal pressure (π_i) possess constant value at lower concentration and increases with increase in stearate concentration for Zn. St – EG system, suggest the close packing of the molecules that indicates solute – solvent interactions. Greater internal pressure favours intramolecular interaction among the components [10]. For Ca. St – EG 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. The absorption coefficient values for binary mixtures Zn. St – EG and Ca. St – EG systems, it shows non linear variation with decrease and increase value as stearate concentration increases. The values of relaxation time (τ) show non linear variation for both the system. 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 [11]. α value increase for Zn. St – EG and Ca. St – EG 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 [12]. The excess velocity (U^E) shows positive deviations predicts the presence of weak interaction which may be due to dispersion force. It shows linear variation in binary mixture Zn. St – EG system and non linear variation for Ca. St – EG 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_f^E) [13]. It also reveals the presence of interstitial accommodation between the components. Increase in compactness between the molecules leading to solute – solvent interaction. In Zn. St – EG system, linear negative deviation indicates that the like molecules are highly packed and disruption of like molecular attraction is less suggesting that structural effects must be considered. Increase in chain length of plasticizers increases steric effect restricting the proper orientation of molecules becomes less compressible. This is confirmed by greater negative deviation in Ca. St – EG systems. It indicates the existence of less molecular interaction between stabilizers and plasticizers. 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. Excess impedance increases with increase in stearate concentration confirms the strong molecular interaction. Among the binary mixtures investigated, Zn. St – EG system shows linear variation predicting the presence of weak physical interaction between them, whereas in Ca. St – EG systems shows non linear variation which identifies strong molecular interaction among them. The excess molar volume (V_m^E) is negative and decrease with increase in stearate concentration for entire composition range. This may be due to strong unlike interactions between molecules. This confirms the presence of partial interstitial accommodation in the empty spaces of stearates by glycols. 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. For both binary mixtures Zn. St – EG and Ca. St – EG systems, deviation follows the order $U_{Vdv} > U_{Jun} > U_{Nom} > U_{Imp}$

International Journal of Innovative Research in Science, Engineering and Technology

An ISO 3297: 2007 Certified Organization

Volume 4, Special Issue 1, February 2015

THIRD NATIONAL CONFERENCE ON ADVANCES IN CHEMISTRY (NCAC – 2015)

On 18th February 2015

Organized by

Department of Chemistry, Easwari Engineering College (SRM Group of Institutions), Chennai-600089, India.

VI. CONCLUSION

The present investigation measures ultrasonic velocity, density and viscosity of stabilizers with plasticizers 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. In Ca. St – EG system, maximum molecular interaction is observed. It predicts the disruption of like forces in glycols and association of both components occurs partially. Comparatively in Zn. St – EG systems shows only weak physical attraction. In comparison among stearates, molecular interaction is greater with calcium stearate than zinc stearate. On the addition of stearate to glycol, the molecular interaction follows the order Ca. St – EG > Zn. St – EG

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 plasticizers. Nomoto and Impedance relation agrees well.

REFERENCES

1. Bahadur Alisha S, Subha M C S and Rao k C . Pure Appl. Ultrason., 23 (2001) 26.
2. Anuradha S, Prema S and Rajagopal KN J. Pure Appl. Ultrason., 27 (2005) 49.
3. Raout B K, Mishra N C, Chakravorty V Indian J. Chem. Technol. 1 (1994) 347.
4. Suhr D, Brummer F, Irmer U, Schlachter M, Hulser Ultrasonics 32 (1994) 301.
5. Pandey J D, Shukla A, Rai R D and Mishra K J J. Chem. Eng. Data., 34 (1989) 29.
6. Roshan Abraham, Abdul Khadar and Jugan J J. Acoust. Soc. Am., 106(3) (1999) 1284.
7. R Kumar, S Jayakumar and V Kannappan., Indian Journal of Pure & Applied Physics., Vol. 46. March 2008, pp. 169 – 175.
8. Ulagendran, R Kumar, S Jayakumar and V Kannappan., Journal of Molecular liquids., 148 (2009) pp. 67 – 72.
9. R Kavitha, S Jayakumar and R Uma ISST Journal of Applied Chemistry, Vol.1, No.2 (2010) 57.
10. R Kavitha, S Jayakumar and R Uma IJESR, Vol.2, Issue 4 (2011) 293.
11. R Kavitha, S Jayakumar and R Uma International Journal of Chemistry and Applications, Vol.3, No.1 (2011) 19.
12. R Kavitha, S Jayakumar and R Uma IOSR Journal of Applied Chemistry, Vol.3, No.2 (2012) 36.
13. R Kavitha, S Jayakumar and R Uma International Journal of Modern Engineering Research, Vol.3, No.1 (2013) 155.