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Ultrasonic Investigation of Binary Mixtures on Stearates and Methyl Ethyl Ketone

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ABSTRACT: *We report the measurements of ultrasonic velocity in the binary mixtures of zinc stearate - methyl ethyl ketone and calcium stearate - methyl ethyl ketone at 303 K. It is 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. From the light of these parameters molecular interaction such as existence of strong molecular association and weak interaction among the participating mixtures has been observed in the present study.*

Keywords: *Stearates, stabilizer, solvent, positive and negative deviation, excess properties.*

I. INTRODUCTION

The velocity of sound in a compound is closely related to many other physical and chemical properties [1]. The self – association of liquids and solids become one of the interesting effects characterizing the solvent. It is especially important when the structure of the solvent plays a crucial role in the studied field [2]. The interest arises, because of the fact that the mixing behaviour of a binary mixture of type A – B is highly dependent upon the geometry, size and structure of both the components [3]. When component A is stearate and the component B is solvent containing aliphatic component, then the molecular interactions of either structure breaking or structure making types are possible. The structure breaking interactions involve mainly the disruptions in the dipolar association in the species. However, the specific interactions that result in the formation of new associated species. For many purposes, it is necessary to know the volumes and compressibility's of the solutions relative to their corresponding values at infinite dilution. The determination of such quantities requires the extrapolation of experimental data in very dilute solutions. Zinc stearate $(C_{18}H_{35}O_2)_2Zn$ and calcium stearate $(C_{17}H_{34}COO)_2Ca$ are the stabilizers used, a soap of zinc and calcium that repels water. It is the most powerful mold release agent among all metal soaps. It contains no electrolyte and has a hydrophobic effect. Its main application areas are the plastics and rubber industry where it is used as a releasing agent and lubricant which can be easily incorporated. Methyl ethyl ketone is used as glue solvents. The polarity, dipole moment, polarizability and hydrogen bonding of a solvent determines what type of components it is able to dissolve and with what other solvents or liquid compounds it is miscible. Therefore, the measurements of physico-chemical property data on such mixtures will be useful in the process engineering. 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.

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 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 ρthe density of mixture and U is is the ultrasonic velocity of the mixture.
The acoustical impedance (Z) was calculated by the equation,

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

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 $K = 1.98 \times 10^{-6}$, 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

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

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

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

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

$$U_{jun} = \left\{ \frac{(X_1V_1 + X_2V_2)}{(X_1M_1 + X_2M_2)^{1/2}} \left[\frac{X_1V_1}{\rho_{1U1}^2} + \frac{X_2V_2}{\rho_{2U2}^2} \right]^{-1/2} \right\} \quad (15)$$

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 X 10^{-1} Nsm^{-2}
Zinc stearate	1404	1133	-
Calcium stearate	1310	1145	-
Methyl ethyl ketone	1170	805	3.97

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 - methyl ethyl ketone and calcium stearate - methyl ethyl ketone 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 / 10^{-1} Nsm^{-2}	β / 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^{-7} m^{3}mole^{-1}
zinc stearate – methyl ethyl ketone									
0.01	1276	811.3	4.09	7.57	1.04	0.97	1.80	0.895	3.84
0.02	1292	817.6	4.26	7.33	1.06	0.97	1.80	0.894	3.73
0.03	1352	823.9	4.43	6.64	1.11	0.99	1.83	0.893	3.81
0.04	1372	830.2	4.60	6.40	1.14	0.99	1.84	0.893	3.72
0.05	1388	836.6	4.77	6.20	1.16	0.99	1.84	0.892	3.62
0.06	1400	842.9	4.94	6.05	1.18	1.00	1.85	0.891	3.51
0.07	1412	849.2	5.12	5.91	1.20	1.00	1.85	0.890	3.40
0.08	1576	855.5	5.29	4.71	1.35	1.04	1.91	0.889	3.85
0.09	1584	861.8	5.47	4.62	1.37	1.04	1.92	0.889	3.73
0.1	1596	868.2	5.65	4.52	1.39	1.04	1.92	0.888	3.62
calcium stearate – methyl ethyl ketone									
0.01	1188	811.0	3.43	8.74	0.964	0.95	1.76	0.895	4.50
0.02	1212	817.1	3.59	8.33	0.990	0.95	1.77	0.894	4.37
0.03	1220	823.2	3.75	8.16	1.00	0.95	1.78	0.893	4.17
0.04	1384	829.2	3.92	6.30	1.15	0.99	1.84	0.893	4.78
0.05	1400	835.3	4.08	6.11	1.17	1.00	1.85	0.892	4.62
0.06	1412	841.4	4.25	5.96	1.19	1.00	1.85	0.891	4.44
0.07	1414	847.4	4.42	5.90	1.20	1.00	1.85	0.890	4.24
0.08	1428	853.5	4.59	5.75	1.22	1.00	1.86	0.889	4.10
0.09	1432	859.6	4.76	5.67	1.23	1.00	1.86	0.889	3.94
0.1	1464	865.6	4.93	5.39	1.27	1.01	1.87	0.888	3.89

Table 3: Thermodynamic parameters of binary mixtures at 303 K

Conc of stearate	$L_f / 10^{-11}$ m	$\pi / 10^6$ atm	$\alpha/f^2 / 10^{-12}$ $m^{-1}s^2$	$\iota / 10^{-10}$ s	$\alpha / 10^{-1}$ m
zinc stearate – methyl ethyl ketone					
0.01	5.46	3.46	6.39	4.13	1.97
0.02	5.30	3.50	6.35	4.16	2.34
0.03	5.11	3.48	5.72	3.92	3.60
0.04	5.02	3.51	5.64	3.92	4.09
0.05	4.94	3.54	5.60	3.94	4.50
0.06	4.88	3.58	5.62	3.99	4.84
0.07	4.82	3.62	5.63	4.03	5.18
0.08	4.30	3.48	4.16	3.32	9.02
0.09	4.27	3.52	4.20	3.37	9.32
0.1	4.22	3.55	4.21	3.41	9.73
calcium stearate – methyl ethyl ketone					
0.01	5.86	3.29	6.64	4.00	0.370
0.02	5.73	3.32	6.49	3.99	0.855
0.03	5.67	3.37	6.60	4.08	1.06
0.04	4.98	3.23	4.68	3.29	4.32
0.05	4.90	3.27	4.68	3.32	4.73
0.06	4.84	3.31	4.71	3.38	5.07
0.07	4.82	3.36	4.85	3.47	5.19
0.08	4.76	3.40	4.85	3.51	5.58
0.09	4.73	3.45	4.96	3.60	5.75
0.1	4.61	3.47	4.77	3.55	6.55

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}	$\beta^E / 10^{-10}$ $Kg^{-1}ms^{-2}$	$Z^E / 10^5$ $Kg\ m^{-2}s^{-1}$	$L_f^E / 10^{-12}$ m	$V_m^E / 10^{-3}$ m^3mole^{-1}
zinc stearate – methyl ethyl ketone					
0.01	106	-1.50	0.928	-5.16	-0.499
0.02	122	-1.74	1.13	-6.03	-0.998
0.03	181	-2.42	1.70	-8.60	-1.50
0.04	201	-2.66	1.95	-9.52	-1.99
0.05	217	-2.85	2.16	-10.3	-2.49
0.06	229	-3.00	2.35	-10.9	-2.98
0.07	241	-3.14	2.53	-11.4	-3.48
0.08	404	-4.34	4.02	-16.6	-3.97
0.09	412	-4.41	4.18	-17.0	-4.46
0.1	424	-4.51	4.38	-17.4	-4.95
calcium stearate – methyl ethyl ketone					
0.01	18	-0.335	0.212	-1.11	-0.472
0.02	42	-0.736	0.475	-2.47	-0.947
0.03	50	-0.902	0.610	-3.05	-1.42
0.04	214	-2.77	2.04	-9.93	-1.89
0.05	229	-2.95	2.25	-10.7	-2.36
0.06	241	-3.09	2.43	-11.2	-2.83
0.07	243	-3.15	2.53	-11.5	-3.30
0.08	257	-3.30	2.73	-12.1	-3.77
0.09	261	-3.37	2.85	-12.4	-4.24
0.1	293	-3.65	3.21	-13.6	-4.71

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 – methyl ethyl ketone									

0.01	1276	1170	1171	1166	1170	-9.032	-8.946	-9.393	-9.029
0.02	1292	1171	1172	1163	1171	-10.372	-10.199	-11.100	-10.366
0.03	1352	1171	1174	1159	1171	-15.469	-15.199	-16.608	-15.458
0.04	1372	1171	1175	1156	1171	-17.147	-16.785	-18.684	-17.132
0.05	1388	1171	1176	1153	1172	-18.484	-18.029	-20.421	-18.464
0.06	1400	1172	1177	1149	1172	-19.479	-18.933	-21.816	-19.453
0.07	1412	1172	1178	1146	1172	-20.473	-19.835	-23.214	-20.441
0.08	1576	1172	1179	1143	1173	-34.433	-33.625	-37.918	-34.390
0.09	1584	1173	1181	1139	1173	-35.082	-34.175	-39.011	-35.031
0.1	1596	1173	1182	1136	1173	-36.072	-35.064	-40.457	-36.013
				calcium stearate – methyl ethyl ketone					
0.01	1188	1170	1171	1167	1170	-1.523	-1.477	-1.832	-1.534
0.02	1212	1170	1171	1163	1170	-3.558	-3.465	-4.189	-3.580
0.03	1220	1171	1172	1160	1170	-4.226	-4.086	-5.177	-4.257
0.04	1384	1171	1173	1157	1170	-18.219	-18.008	-19.653	-18.265
0.05	1400	1171	1173	1153	1170	-19.568	-19.303	-21.374	-19.625
0.06	1412	1171	1174	1150	1170	-20.574	-20.256	-22.754	-20.642
0.07	1414	1171	1175	1147	1170	-20.727	-20.358	-23.267	-20.804
0.08	1428	1171	1175	1144	1171	-21.904	-21.481	-24.827	-21.991
0.09	1432	1172	1176	1141	1171	-22.227	-21.754	-25.513	-22.323
0.1	1464	1172	1177	1138	1171	-24.940	-24.406	-28.661	-25.046

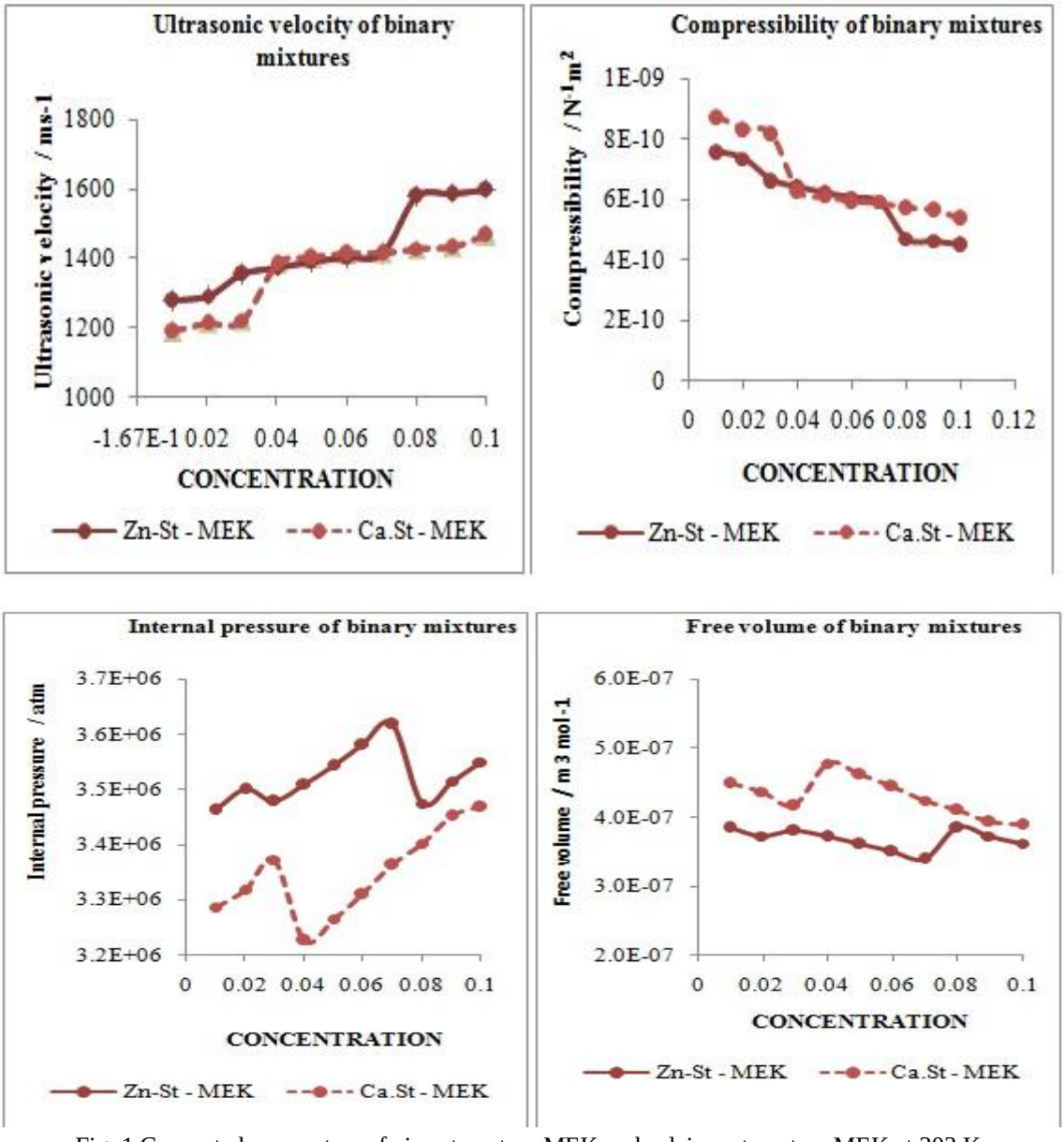

Fig. 1 Computed parameters of zinc stearate – MEK and calcium stearate – MEK at 303 K

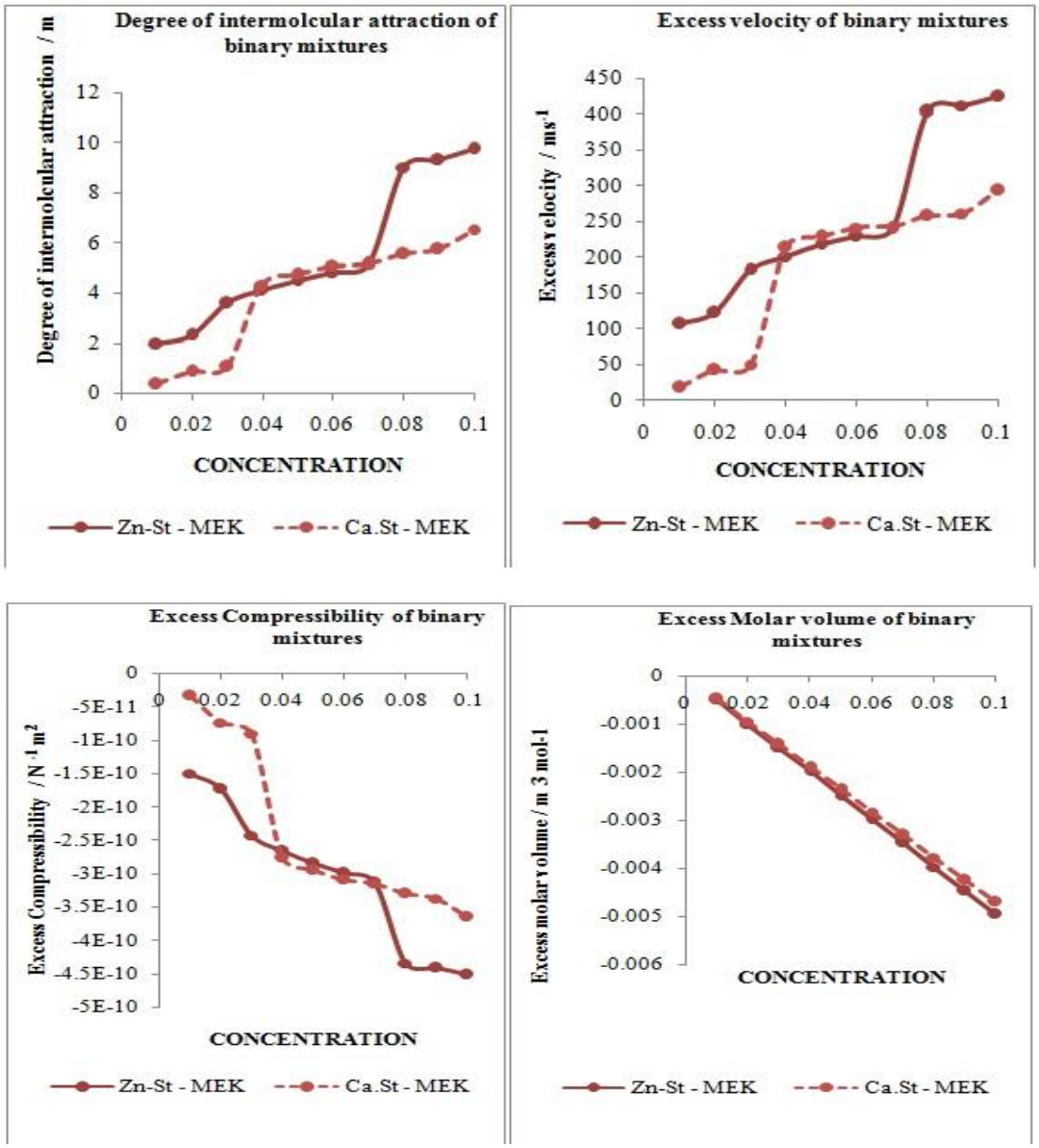

Fig. 2 Excess parameters of zinc stearate – MEK and calcium stearate – MEK at 303 K

The ultrasonic velocity values (U) increases linearly with increase in concentration of stearates zinc stearate, calcium stearate in addition to methyl ethyl ketone. Increase in concentration of either zinc stearate or calcium stearate favours increase in ultrasonic velocity due to decrease in space between chains inside the structure of material, thus decrease in spacing may be attributed to increase in cross linking between chains which consequently cause increase in rigidity of the material. When kinetic elements of adjacent chains have high mobility, cross linkages prevent the moving part of adjacent chains increase effectiveness of intermolecular interaction. This may result in a growth in the modulus of elasticity of stearates and ultrasonic velocity with increase in cross linkage factor. However, ultrasonic velocity increases as stearates behave as weak electrolytes in dilute solution and ionize into simple metal cations as either Zn^{2+} and $RCOO^{-}$ or Ca^{2+} and $RCOO^{-}$. Methyl ethyl ketone used in the present study depends upon polarity, increase in polarity due to the high electro negativity increases molecular motion leading to solute – solvent interaction [4]. It is observed that slight increase in addition of zinc stearate with methyl ethyl ketone than with calcium stearate – methyl ethyl ketone, but after 0.04M concentration, it shows similar trend of increase with increase in stearate concentration. The density values (ρ) increases with increase in concentration predicts that there is greater molecular interaction between the two components [5]. The viscosity values (η) increases with increase in concentration which give some reliable information in the study of molecular interaction [6]. As concentration increases, association increases or sterric crowding is more so that the intermolecular interaction between the molecules is weakened.

The adiabatic compressibility (β) exhibits an exact reverse trend as that of ultrasonic velocity. The disruption of stearates by solvents and weak interaction between unlike molecules leave the binary mixtures more compressible. When stearates are added to methyl ethyl ketone, it attracts certain solvent molecules towards itself by wrenching the molecule from bulk of the solvent due to the force of electrostriction. The available solvent molecules for the next incoming component get decreased and every solvent has a limit for the compression as limiting compressibility value. The

compressibility of solvent is greater than that of solution and it decreases with increase in concentration of solution [7] shows non – linear variation in both zinc stearate – methyl ethyl ketone and calcium stearate – methyl ethyl ketone. Acoustic impedance increases with increase in stearate concentration due to the interaction between stearate and solvent molecules which increases intermolecular distance making relatively wider gaps between the molecules and becoming the main cause of impediment in the propagation of ultrasonic waves. It is observed that linear increase in acoustic impedance with increase in concentration of either zinc stearate or calcium stearate confirms the presence of molecular association between solute – solvent molecules through intermolecular hydrogen bonding [8]. Rao constant (R) and Wada's constant (W) shows linear variation and almost it is constant with increase in concentration which indicates the presence of solute – solvent interaction. In mixtures zinc stearate – methyl ethyl ketone and calcium stearate – methyl ethyl ketone, decrease in the free volume is observed. It also confirms the increasing order of symmetry and presence of close packing nature in the systems.

The intermolecular free length (L_f) also follows the same trend as that of adiabatic compressibility. The decrease in free length with increase in ultrasonic velocity along with increase in concentration of zinc stearate or calcium stearate in binary mixtures leads to increase in intermolecular force, which strengthens the idea of molecular association in each system [9]. In both the binary mixtures zinc stearate – methyl ethyl ketone and calcium stearate – methyl ethyl ketone greater free length is predicted.

For the binary mixtures zinc stearate – methyl ethyl ketone and calcium stearate – methyl ethyl ketone, the association between like molecules is weak unlike molecular interaction at specific concentration which leads to the very low contribution to the internal pressure values. The change in the values of internal pressure is very low which suggests that weak interaction is present and which is almost concentration independent. Increase in internal pressure with decrease in free volume along with increase in concentration of stearate suggest the close packing of the molecules inside the shield, which may be brought about by increase in magnitude of interactions.

The absorption coefficient values (α/f^2) in binary mixtures zinc stearte – methyl ethyl ketone and calcium stearate – methyl ethyl ketone decreases and increases with variation in concentration. The values of relaxation time are calculated shows both increase and decrease with increase in concentration of either zinc stearate or calcium stearate to methyl ethyl ketone. Intermolecular attraction is the study of the structural variation and the nature of interaction occurring in the system. Maximum value confirms the presence of intermolecular interaction in system. In addition of zinc stearate – methyl ethyl ketone and calcium stearate – methyl ethyl ketone interaction parameter (α) value increases with increase in concentration shows molecular interaction between them [10]. Large positive value of interaction parameter yields weakening of molecular forces. The strengthening of molecular forces is represented by negative values of molecular interaction parameter.

The computed values of excess parameters for the mixtures at temperature 303 K are given in Table 5 and the plots of excess parameters versus concentration are shown in Fig.1 & 2. The excess velocity shows positive deviations which predict the weak interaction due to dispersion force. It shows non linear variation for zinc stearate – methyl ethyl ketone and calcium stearate –methyl ethyl ketone, predicting specific intermolecular interaction between them, leads to strong association due to rupture of cohesion and growing adhesion forms dipole – dipole interaction. Non linear increase and decrease values are observed with respect to the concentration of stearates. In all binary mixtures, it shows large deviation at high concentration implies that the specific interaction dominate over the dispersive interaction between unlike molecules. However decrease in excess compressibility with increase in ultrasonic velocity suggests that there may be strong intermolecular hydrogen bond existing between them making the binary mixture less compressible indicate significant interaction [11]. The negative excess free length values investigated are resultant of several opposing factors such as strong molecular interaction through charge transfer, dipole – induced dipole and dipole – dipole interaction, interstitial accommodation and orientation ordering lead to a more compact structure.

It was reported that the positive deviation in excess ultrasonic velocity and excess impedance indicates the presence of strong interactions between component molecules in the mixture. Excess impedance increases with increase in concentration of either zinc stearate or calcium stearate with addition of solvents confirms the strong molecular interaction.

Excess values may be affected by three factors, first factors explains the specific forces between molecules such as hydrogen bond, charge transfer complex shows large negative deviation. The second factor deals with the physical intermolecular forces, including electrostatic forces between charged particles, between a permanent dipole, induction forces between a permanent dipole and an induced dipole, force of attraction and repulsion between non polar molecules favouring physical intermolecular force shows both positive and negative deviation. The third factor deals with the structural characteristics of the component arising from geometrical fitting of one component into other structure due to the differences in shape and size of the components. Excess molar volume shows negative deviation in the binary mixtures and linear decrease with increase in concentration of either zinc stearate or calcium stearate. Increase in chain length and increase in polarizability decreases excess molar volume that can be attributed to strong unlike interactions between molecules.

The experimental and theoretical velocities calculated by using various empirical relations are presented in Tables 5 for the binary mixtures at temperature 303 K. It is assumed that all the liquid molecules are spherical in shape which is not true every time, it is supposed that volume does not change on mixing. The deviation factor from the calculated and experimental values of ultrasonic velocity is reasonable and provides very good agreement with experimental value. The observed deviation of theoretical values of velocity from the experimental values should be rather treated as evidence of molecular interaction which takes place between the component molecules in the binary system. Deviation is larger in Van Dael and Vangeel relation due to strengthening among unlike molecules. At all concentrations experimental ultrasonic velocity is found to be in good agreement with theoretical Nomo to velocity which is due to weak dipolar dispersive interaction between like molecules. The agreement between experimental and theoretical velocity follows the order

$U_{Nom} > U_{Jun} > U_{Imp} > U_{Vdv.}$ Thus the observed deviation of theoretical values of velocity from the experimental values shows that the molecular interaction is taking place between the solute molecules in stearate and solvent [12]. Comparatively zinc stearate – methyl ethyl ketone shows maximum deviation that confirms strong molecular interaction and calcium stearate – methyl ethyl ketone shows least deviation revealing weak interaction among them. The less deviation in Nomoto's relation suggests that the interactions are due to dipole – dipole, dipole – induced dipole between like molecules. At all concentrations Van Dael and Vangeel velocity value shows maximum deviation. This may not be due to the weak dipolar and dispersive interactions between the like molecules. As the availability of free dipoles increases, the dipole induced dipole interaction dominates [13-14].

IV. CONCLUSION

The present investigation of stabilizers zinc stearate, calcium stearate with solvent methyl ethyl ketone and its experimental values of ultrasonic velocity, density and viscosity for the binary mixtures of zinc stearate - methyl ethyl ketone and calcium stearate - methyl ethyl ketone at 303 K are measured. When aliphatic ketone methyl ethyl ketone is added to either zinc stearate or calcium stearate, interaction is less. It may be due to the reason that both are aliphatic components.

zinc stearate – methyl ethyl ketone ≈ calcium stearate – methyl ethyl ketone

Among the binary mixtures, solvents in addition to zinc stearate show maximum molecular interaction than with calcium stearate may be due to the presence of zinc ion. The theoretical velocities obtained by various theories also well reflect the existing interactions. From these data, thermodynamic excess functions have been calculated and correlated using standard relations like Impedance relation, Nomo to relation, Van Dael & Vangeel and Junjie theory. The sign and magnitude of these quantities have been discussed in terms of dipole – induced dipole interactions between the mixing components.

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