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Molecular Interaction Studies on Binary Liquid Mixture of Ethyl Oleate and Ethyl Methyl Ketone at Temperature Range from 303.15K to 318.15K

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***Abstract*: Density (ρ), ultrasonic velocities (u) and dynamic viscosity (η) for binary mixture of Ethyl oleate with Ethyl methyl ketone is experimented at ambient temperature range from 303.15K to 318.15K at atmospheric pressure over various compositions. The density (ρ) and viscosity (η) are calibrated using Specific gravity bottle and Ostwald's glass capillary viscometer respectively. The velocity (U) is measured using ultrasonic interferometer. The thermo dynamic parameters such as internal pressure (πi), free volume (V_f), Molar volume (V_m) and acoustical parameters such as adiabatic compressibility (β), inter molecular free length (L_f), acoustic impedance (z), relaxation time (τ) and their excess parameters have been calculated.**

Keywords: Ultrasonic velocity, density, viscosity, adiabatic compressibility, free volume, internal pressure, molecular interactions.

INTRODUCTION

In our earlier investigations, [1-2] we made an attempt by making use of an ultrasonic technique to explore the behavior of some of the amino acids as well as in organic liquid mixtures. In recent years much effort has been made with measurement and interpretation of the ultrasonic properties of liquids and liquid mixtures. The ultrasonic studies are of great importance in helping to understand the nature and extent of the patterns of molecular aggregation that exist in liquid mixtures, resulting from intermolecular interactions [3-4].There has been an increasing interest in the study of systems comprising of unlike components with interactions of varying type. The sign and magnitude of excess parameters have been used to investigate the interactions between the components of a system [5-7].

Molecular interactions are interactions between electrically neutral molecules or atoms. Other than atomic bonds these are electrical in nature and consist of attractive forces (orientation, induction, and dispersion forces) and repulsive forces. Molecular interaction first taken into consideration by J. D. van der Waals (1873) in explaining the properties of real gases and liquids. These depend on the distance between the molecules and usually are described by the potential energy of interaction. Studies on liquid- liquid mixtures either binary, ternary or more has importance of its own in various fields of con temporal civilized societies like chemical engineering, food processing, preparation of cosmetics, polymer paints and cleansing agents, petroleum, edible and non edible oil, preparation of bio diesel etc. Ultrasonic waves have their extensive applications in various fields like nondestructive tests for solids and liquids in medical and engineering, food processing, pharmaceutical, polymer and chemicals, metallurgical industries etc. It will be an advantageous tool if these two fields were combined for conducting studies on inter and intra particulate behavior. Ultrasonic investigations of binary mixtures have been taking place since decades by so many scholars under various heads like acoustic, thermodynamic, molecular interactions etc. The thermodynamic studies of binary liquid mixtures have attracted much attention of research scholars and scientists, and experimental data on number systems are available from review and publication [8-12]. Ultrasonic investigation of liquid mixtures consisting polar and non-polar components is of considerable importance in understanding intermolecular interaction between the component molecules and they find applications in a number of industrial and technological processes. Many investigations [13-18] have been employed in the task of collecting more and more data and explaining in terms of the properties of pure liquid. In the present paper the author submitting part of the studies as the effect of temperature and concentration on ultrasonic velocity(v) of 2MHz wave in the pure and mixtures of two organic liquids Ethyl Oleate and Ethyl Methyl Ketone at various temperatures 303.15K, 308.15K, 313.15K and 318.15K. The effects on density (ρ), viscosity (η), Adiabatic compressibility (βad), Inter molecular free length (Lf) and Internal pressure (Πi) also were studied. Results were tabulated and the relations among the mentioned parameters were represented as Graph.1-24.

MATERIALS AND EXPERIMENTS

All the materials procured are of Sigma-Aldrich AR grade and glassware used of Borosilicate make. Organic liquids Ethyl Oleate and Ethyl Methyl Ketone were procured are used directly without any purification. The densities and viscosities of the liquid compounds were measured with specific gravity bottle and Ostwald viscometer pre calibrated with 3D [19] water of

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Millipore to nearest mg/ml. The time taken for flow of viscous fluid in Ostwald viscosity meter is measured to a nearest 0.01 sec. Borosilicate glassware, Japan make Shimadzu electronic balance of sensitivity +0.001gm and constant temperature water bath of accuracy +0.1K were used while conducting the experiments. 2MHz ultrasonic interferometer model no. F-05 with least count of digital micrometer 0.001mm of Mittal Enterprises [20] was used for calculating velocities of sound waves and all the tests were conducted as per ASTM standard [21] procedures. The 30ml of binary mixtures of Ethyl Oleate and Ethyl Methyl Ketone were prepared with variable volumes of 5ml each to conduct the experiments from which the mole fractions were calculated [22].

THEORY AND CALCULATIONS

In order to examine the inter molecular interactions in liquid mixtures of Ethyl Oleatae with Ethyl Methyl Ketone, experiments were conducted to find the density, viscosity and velocity of 2MHz ultrasonic waves for pure liquids and for binary liquid mixtures. The results of pure liquids are compared with literature values for assessment. From the experimental data of binary mixtures, the derived and excess values were calculated at various mole fractions of Ethyl Oleatae for understanding the inter and intra molecular interactions at each temperature. The derived and excess values are calculated by using the fallowing relations.

Adiabatic compressibility (β_{ad})

Adiabatic compressibility the parameter which represents the ability to change volume of a liquid sample is

$$\beta_{ad} = (\rho\, U^2)^{-1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Intermolecular free length (L_f)

The formula for outer to outer distance between the interacting molecules

$$L_f = K\sqrt{\beta_{ad}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Molar volume of the binary liquid mixture (V_m)

The molar volume of the system at every mole fraction for the mixture is given by

$$V_m = M_{eff}/\rho_{mix} \text{ where } M_{eff} = M_1 X_1 + M_2 X_2 /(X_1 + X_2) \ldots\ldots\ldots (3)$$

Free volume (V_f)

The free volumes of the binary mixtures have been computed using its relationship with the ultrasonic velocity and viscosity as given below

$$V_f = \left(\frac{MU}{K\eta}\right)^{\frac{3}{2}} \qquad \ldots\ldots\ldots\ldots (4)$$

Where k is a constant, which is independent of temperature and its value is 4.28 X 10^9 for all liquids.

Specific acoustic impedance (Z)

The ultrasonic velocity is influenced by the acoustic impedance (Z), which is given by the relation

$$Z = \rho U \qquad \ldots\ldots\ldots\ldots\ldots (5)$$

EXCESS THERMODYNAMIC PARAMETERS

With the help of excess parameters the extent of deviation from the ideal behavior of binary mixture can be estimated. The difference between the thermodynamic function of mixing for a real system and the value corresponding to a perfect solution at the same temperature, pressure and composition is called the thermodynamic excess function, denoted by Y^E.

Excess value Y^E for each parameter can compute by using the general formula

$$Y^E = Y - (Y_1 X_1 + Y_2 X_2) \qquad \ldots\ldots\ldots\ldots\ldots (6)$$

Where Y is the parameter under consideration, X_1 and X_2 are mole fractions of two liquids Ethyl Oleate and other organic compound under consideration respectively of the binary system, Ethyl Methyl Ketone here and E represent 'excess'.

Deviation in adiabatic compressibility ($\Delta\beta_{ad}$)

The difference of the adiabatic compressibility of the mixture and the sum of the fractional contributory adiabatic compressibility's of the two liquids individually is the deviation in adiabatic compressibility. At a given mole fraction it is given by

$$\Delta\beta_{ad} = \beta_{ad} - (\beta_{ad1} X_1 + \beta_{ad2} X_2) \ldots\ldots\ldots\ldots\ldots (7)$$

Excess free length (L_f^E)

The excess free length can be calculated with formula

$$L_f{}^E = L_f - (L_{f1} X_1 + L_{f2} X_2) \qquad \ldots\ldots\ldots\ldots\ldots (8)$$

Excess acoustic impudence (Z^E)

Excess acoustic impedance can be calculated by the relation

$$Z^E = Z - (Z_1 X_1 + Z_2 X_2) \qquad \ldots\ldots\ldots (9)$$

RESULTS AND DISCUSSION

Velocities of 2MHz ultrasonic wave, densities and viscosities of pure Ethyl Oleate and Ethyl Methyl Ketone were measured with pre calibrated interferometer, specific gravity bottle and Ostwald viscometer respectively in the temperature range of 303.15K to 318.15K. The results were compared with available literature and shown in table.1 and table.2. The experimental

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values of density (ρ), viscosity (η) and speed of sound (u) for all the mixtures over the entire range of composition and at 303.15K, 308.15K, 313.15K and 318.15 K are presented in table3, table4 and table5.

Table.1. Comparison of experimental and literature values of density (ρ), viscosity (η) and velocity (U) of 2MHz ultrasonic wave of pure Ethyl oleate

Parameter	303.15K		308.15K		313.15K		318.15K	
	Expt.	Lite.	Expt.	Lite.	Expt.	Lite.	Expt.	Lite.
Density(ρ) kg/m^3	863.54	863.20[23]	859.32	859.50[23]	855.56	855.80[23]	852.10	855.20[23]
Viscosity (η) Ns/m^2	5.3100	5.3094[23]	4.7164	4.7156[23]	4.2165	4.2137[23]	3.6698	3.7876[23]
Velocity (U) m/s	1368.16	1360.67[24]	1340.78	1342.98[24]	1324.02	1325.49[24]	1305.04	1308.17[24]

Table.2. Comparison of experimental and literature values of density (ρ), viscosity (η) and velocity (U) of 2MHz ultrasonic wave for pure Ethyl methyl ketone

Parameter	303.15K		308.15K		313.15K		318.15K	
	Expt.	Lite.	Expt.	Lite.	Expt.	Lite.	Expt.	Lite.
Density (ρ) kg/m^3	794.3	794.0[25]	789.6	788.8[26] 784.6[29]	783.2	783.1[27]	777.4	778.5[28]
Viscosity (η) Ns/m^2	0.3690	0.362[26]	0.3460	0.346[27]	0.3351	0.330[28]	0.3170	0.316[28]
Velocity (U) m/s	1171.6	1170.6[30]	1154.9	1153.8[26]	1122.6	1120.4[30]	1097.8	1096.4[26]

Table.3. Ultrasonic Velocity (U), Density (P), Viscosity (H), Adiabatic Compressibility (β_{ad}), Inter Molecular Free Length (L_f), Molar Volume (V_m), Rao's Constant(R), Wada's Constant (W) for Binary Mixture Of Ethyl Oleate and Ethyl Methyl Ketone at different temperatures.

Mole fraction (X1)	Mole fraction (X2)	Velocity m/sec (U)	Density Kg/m3 (ρ)	Viscosity Nsm-2 (η)	Ad. Comp. 10^{-10} N-1.m2 (βad)	Int. Mol. Free length 10^{-10} m (Lf)	Mol. Vol. (Vm)	Rao'sConstnt (R)	Wada's Constant (W)
T= 303.15 K									
0.0000	1.0000	1171.6	794.3	0.369	9.1718	6.2841	90.781	4.4421	6.6145
0.0480	0.9519	1204.36	805.84	1.1925	8.5553	6.0692	103.7	5.1211	7.6314
0.1120	0.8879	1237.12	817.38	2.016	7.9937	5.8667	120.91	6.0246	8.9845
0.2017	0.7984	1269.88	828.92	2.8395	7.4810	5.6754	144.96	7.2864	10.874
0.3351	0.6645	1302.64	840.46	3.663	7.0118	5.4945	180.97	9.1737	13.702
0.5797	0.442	1335.4	852	4.4865	6.5816	5.3233	240.77	12.307	18.395
1.0000	0.0000	1368.16	863.54	5.31	6.1864	5.1610	359.59	18.529	27.717
T=308.15 K									
0.0000	1.0000	1154.9	789.6	0.346	9.4952	6.4556	91.321	4.4472	6.621
0.0481	0.9519	1185.88	801.22	1.0744	8.875	6.2412	104.31	5.1249	7.6363
0.1122	0.8878	1216.86	812.84	1.8028	8.3083	6.0387	121.61	6.0265	8.9872
0.2017	0.7983	1247.84	824.46	2.5312	7.7896	5.8471	145.8	7.2856	10.874
0.3357	0.6643	1278.82	836.08	3.2596	7.3136	5.6657	181.98	9.1685	13.696
0.5582	0.4418	1309.8	847.7	3.988	6.8762	5.4936	242.06	12.293	18.378
1.0000	0.0000	1340.78	859.32	4.7164	6.4734	5.3303	361.36	18.495	27.673
T=313.15 K									
0.0000	1.0000	1122.6	1122.6	0.3351	10.132	6.7321	92.067	4.4413	6.6136
0.0483	0.9517	1156.17	1156.1	0.982	9.4069	6.4869	105.15	5.1223	7.6336
0.1126	0.8874	1189.74	1189.7	1.6289	8.7508	6.2566	122.56	6.0277	8.99
0.2023	0.7977	1223.31	1223.3	2.2758	8.1553	6.0399	146.88	7.2912	10.883
0.3366	0.6634	1256.88	1256.8	2.9227	7.6134	5.8358	183.24	9.1787	13.711
0.5591	0.4409	1290.45	1290.4	3.5696	7.1192	5.6432	243.53	12.306	18.398
1.0000	0.0000	1324.02	1324.0	4.2165	6.6675	5.4612	362.95	18.499	27.678
T=318.15 K									
0.0000	1.0000	1097.8	777.4	0.317	10.673	6.9751	92.754	4.4413	6.6135
0.0484	0.9515	1132.34	789.85	0.8758	9.8741	6.7089	105.91	5.124	7.6362
0.1128	0.8871	1166.88	802.3	1.4346	9.1539	6.4596	123.42	6.0313	8.9955
0.2028	0.7971	1201.42	814.75	1.9934	8.5032	6.2257	147.87	7.2965	10.891
0.3373	0.6626	1235.96	827.2	2.5522	7.9137	6.006	184.4	9.1851	13.722

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0.5599	0.4400	1270.5	839.65	3.111	7.3782	5.7993	244.88	12.311	18.406
1.0000	0.0000	1305.04	852.1	3.6698	6.8906	5.6044	364.42	18.485	27.66

Table.4.Freee Volume (V_f), Acoustic Impedance (Z), Internal Pressure(Π),Gibb's Energy (G^E), Enthalpy(H) and Relaxation Time(T) for binary mixture of Ethyl Oleate and Methyl ketone at different temperatures.

Mole fraction (X_1)	Mole fraction (X_2)	Free Volume (V_f)	Acoustic Impedance (Z)	Internal pressure (π)	Gibb's Energy (G^E)	Enthalpy (H)	Relaxation time (τ)
T=303.15 K							
0.0000	1.0000	3.9109	0.9306	341.26	0.1065	30.980	0.45125
0.0480	0.9519	0.8753	0.9705	514.36	0.11062	53.339	1.3603
0.1120	0.8879	0.5332	1.0112	547.74	0.11232	66.227	2.14873
0.2017	0.7984	0.4448	1.0526	515.58	0.11335	74.7412	2.83232
0.3351	0.6645	0.4491	1.0948	443.26	0.11406	80.217	3.4246
0.5797	0.442	0.5386	1.1378	344.89	0.11458	83.039	3.93717
1.0000	0.0000	0.8079	1.1815	230.59	0.11498	82.919	4.38003
T=308.15 K							
0.0000	1.0000	4.2155	0.9119	336.99	0.1082	30.775	0.438
0.0481	0.9519	1.0003	0.9502	498.14	0.1122	51.962	1.2714
0.1122	0.8878	0.6153	0.9891	528.76	0.114	64.305	1.9971
0.2017	0.7983	0.515	1.0288	497.19	0.115	72.488	2.6289
0.3357	0.6643	0.5207	1.0692	427.31	0.1157	77.763	3.1786
0.5582	0.4418	0.6246	1.1103	332.51	0.1163	80.487	3.6563
1.0000	0.0000	0.9364	1.1522	222.42	0.1167	80.374	4.0708
T=313.15 K							
0.0000	1.0000	4.2386	0.8792	339.99	0.1102	31.302	0.4527
0.0483	0.9517	1.1028	0.9195	487.43	0.114	51.251	1.2317
0.1126	0.8874	0.6936	0.9605	513.67	0.1157	62.954	1.9006
0.2023	0.7977	0.5874	1.0024	481.2	0.1167	70.677	2.4747
0.3366	0.6634	0.5987	1.045	412.6	0.1174	75.604	2.9669
0.5591	0.4409	0.7225	1.0885	320.61	0.1179	78.076	3.3884
1.0000	0.0000	1.087	1.1328	214.44	0.1183	77.83	3.7484
T=318.15 K							
0.0000	1.0000	4.45496	0.8534	338.053	0.11196	31.3558	0.45114
0.0484	0.9515	1.26994	0.8944	470.176	0.11563	49.7979	1.15304
0.1128	0.8871	0.81607	0.9362	492.017	0.11727	60.7266	1.75098
0.2028	0.7971	0.69855	0.9789	459.376	0.11827	67.9284	2.26006
0.3373	0.6626	0.71673	1.0224	393.13	0.11895	72.4913	2.69299
0.5599	0.4400	0.86871	1.0668	305.182	0.11945	74.7335	3.06049
1.0000	0.0000	1.31007	1.112	204.169	0.11983	74.4032	3.37165

Table.5. Excess Velocity, Excess Adiabatic Compressibility ($\Delta\beta_{ad}$), Excess Inter Molecular Free Length (L_f^e), Excess Impedance (Z^E), Excess Molar Volume (V_m^E), Excess Free Volume(V_f^E), Excess Viscosity (ΔH),Excess internal pressure (Π^E), Excess Gibbs Energy(ΔG^E), Excess Enthalpy (H^E) for binary mixture of Ethyl oleate and Ethyl Methyl ketone at different temperatures.

(X_1)	U^E	$\Delta\beta_{ad}$	L_f^E	Z^E	V_m^E	V_f^E	Δη	Π^E	ΔG^E	H^E
T=303.15 K										
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0480	23.312	-0.473	-0.1609	0.0278	-0.0608	-2.8864	0.58602	178.41	0.0280	19.862
0.1120	43.489	-0.8435	-0.2916	0.0528	-0.1415	-3.0299	1.09321	218.88	0.0386	29.425
0.2017	58.659	-1.0891	-0.3823	0.0714	-0.2423	-2.8407	1.47455	196.62	0.0426	33.291
0.3351	65.092	-1.1584	-0.4128	0.0800	-0.4427	-2.4207	1.63626	139.13	0.0410	31.810
0.5797	54.126	-0.9244	-0.3341	0.0671	-0.3341	-1.6409	1.36059	65.377	0.0306	23.0784
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T=308.15 K										
0.0000	0.0000	0.0000	0.0000	0.0000	0	0.0000	0.0000	0.0000	0.0000	0.0000
0.0481	22.037	-0.4748	-0.1603	0.0267	-0.0902	-3.0575	0.5181	166.66	0.0275	18.801
0.1122	41.107	-0.8479	-0.2907	0.0503	-0.1806	-3.2323	0.9665	204.62	0.0382	27.966
0.2017	55.442	-1.096	-0.3815	0.0684	-0.2814	-3.039	1.3035	183.3	0.0424	31.707

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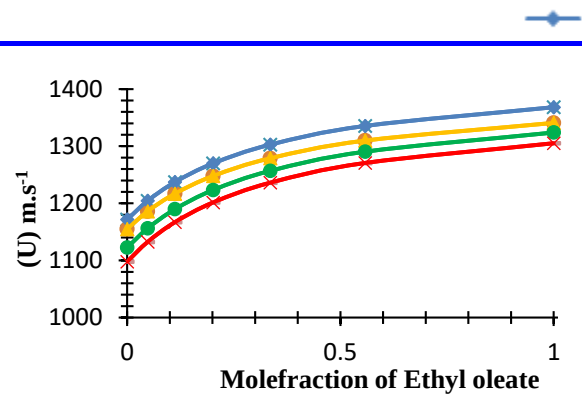
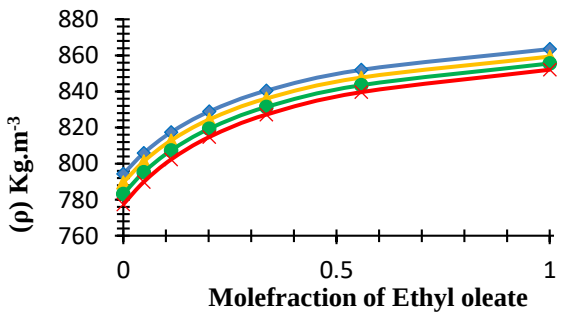
0.3357	61.513	-1.167	-0.4121	0.0766	-0.4662	-2.5939	1.4463	128.78	0.0408	30.336
0.5582	51.138	-0.9322	-0.3338	0.0643	-0.3437	-1.7604	1.2023	59.468	0.0306	22.024
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T=313.15 K										
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0483	23.845	-0.5574	-0.1839	0.028	-0.1224	-2.9836	0.4595	153.504	0.0265	17.7032
0.1126	44.469	-0.9908	-0.3325	0.0527	-0.2224	-3.1903	0.8569	187.817	0.0371	26.4153
0.2023	59.955	-1.2753	-0.435	0.0718	-0.3250	-3.0135	1.1553	166.616	0.0414	29.9609
0.3366	66.487	-1.3522	-0.4685	0.0805	-0.4885	-2.5791	1.2812	114.865	0.0401	28.6415
0.5591	55.227	-1.0754	-0.3783	0.0675	-0.3682	-1.7539	1.0642	50.8176	0.0300	20.7588
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T=318.15 K										
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0484	24.501	-0.6161	-0.1999	0.0284	-0.1598	-3.0326	0.3964	138.608	0.0255	16.3569
0.1128	45.684	-1.0925	-0.3608	0.0536	-0.2608	-3.2838	0.7391	169.078	0.0360	24.5109
0.2028	61.574	-1.4028	-0.4713	0.073	-0.3612	-3.1183	0.9962	148.486	0.0404	27.8389
0.3373	68.251	-1.4837	-0.5067	0.0817	-0.5066	-2.6773	1.1042	100.24	0.0392	26.6143
0.5599	56.65	-1.177	-0.4083	0.0685	-0.4082	-1.8251	0.9165	42.1016	0.0295	19.272
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

In order to examine the inter molecular interactions in liquid mixtures of Ethyl Oleate with Ethyl methyl ketone experiments were conducted to find the density, viscosity and velocity of 2MHz ultrasonic waves for pure liquids and for liquid mixtures. The results of pure liquids are compared with literature values. The experimental values are coinciding with the values from the previous studies. The derived, excess values were calculated at various mole fractions of Ethyl Oleate for understanding the inter and intra molecular interactions at each temperature. Graphs were drawn for variation of the experimental and derived quantities with mole fraction of Ethyl Oleate at all the study temperatures as shown in graph 1 to graph 24. From the above studies it can be concluded that there exists a dipole-dipole interactions among the unlike molecules.



Graph 1 Ultrasonic Velocity VsMolefraction of Ethyl Oleate (X_1)



Graph 2 Density Vs Mole fraction of Ethyl Oleate (X_1)

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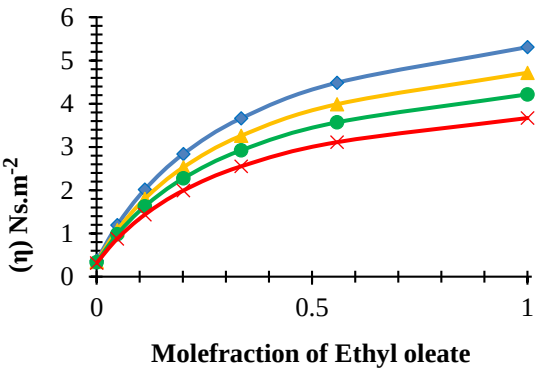
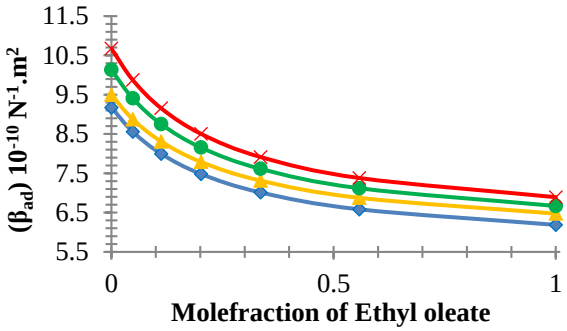
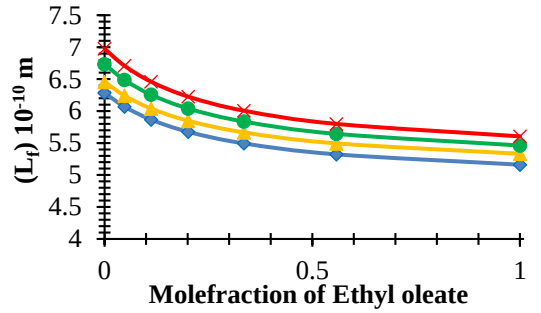


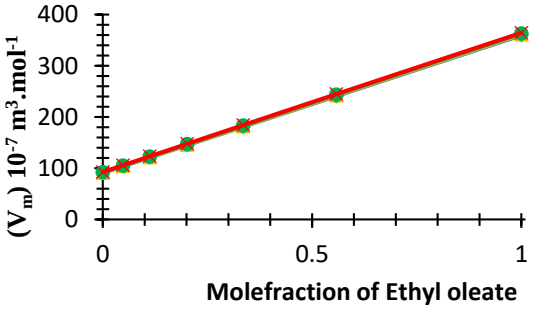
Graph.3 Viscosity Vs Mole fraction of Ethyl Oleate (X_1)



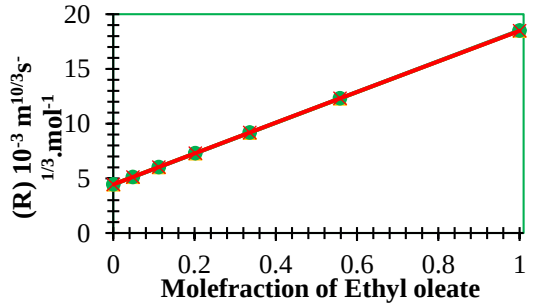
Graph 4 Adiabatic Compressibility VS Mole fraction of Ethyl Oleate (X_1)



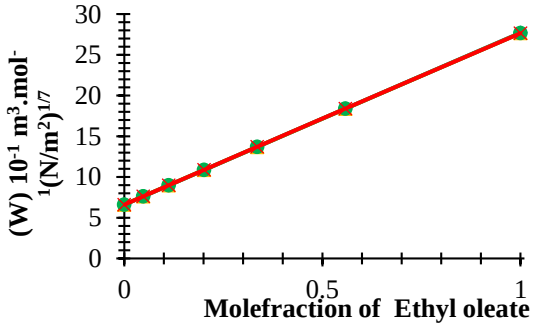
Graph 5 Intermolecular freelengthVs Mole fraction of Ethyl Oleate (X_1)



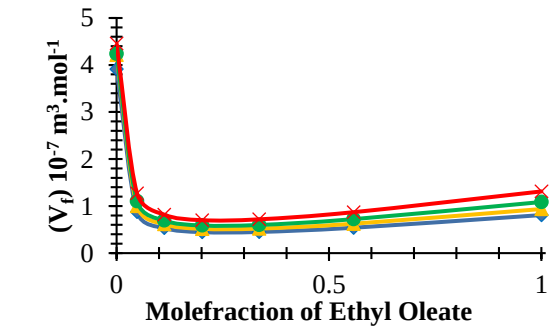
Graph 6 Molar Volume Vs Mole fraction of Ethyl Oleate (X_1)



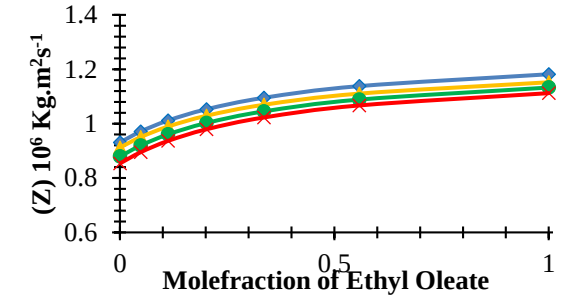
Graph 7 Rao's Constant Vs Mole fraction of Ethyl Oleate (X_1)



Graph 8 Wada's Constant Vs Mole fraction of Ethyl Oleate (X_1)



Graph 9 Free Volume Vs Mole fraction of Ethyl Oleate (X_1)



Graph 10 Acoustic Impedance Vs Mole fraction of Ethyl Oleate (X_1)

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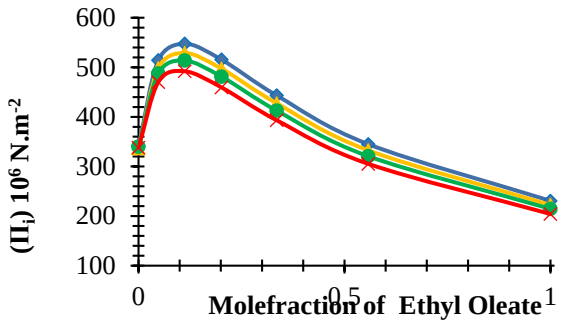
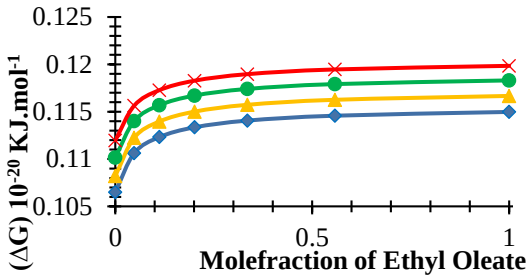
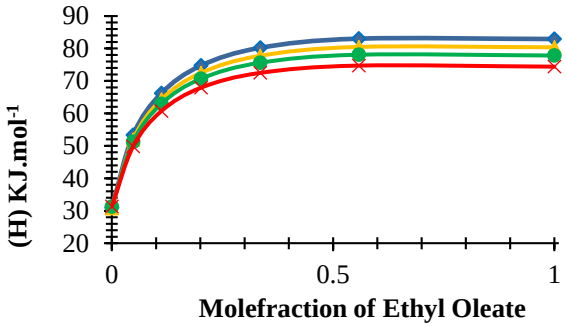


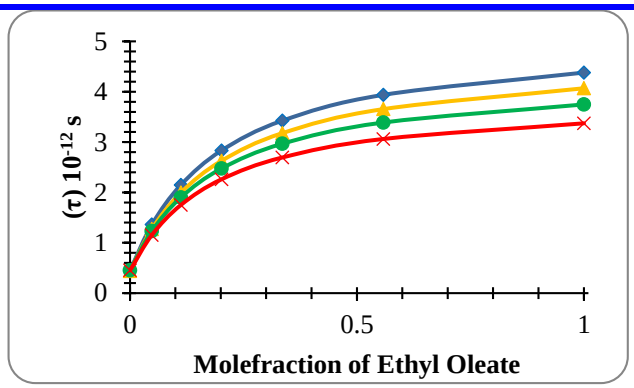
Graph 11 Internal Pressure Vs Mole fraction of Ethyl Oleate (X_1)



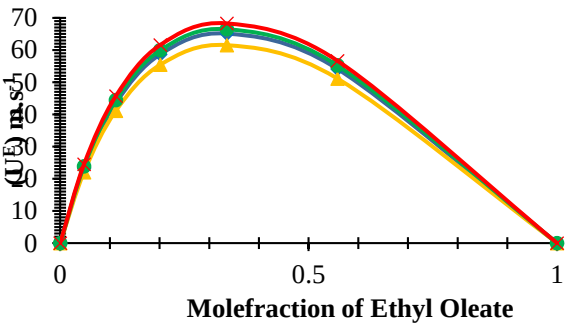
Graph 12 Gibb's Free Energy Vs Mole fraction of Ethyl Oleate (X_1)



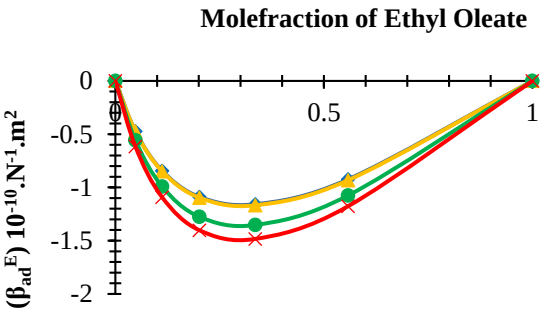
Graph 13 Enthalpy Vs Mole fraction of Ethyl Oleate (X_1)



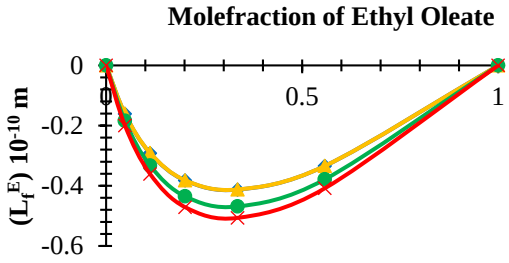
Graph 14 Relaxation Time Vs Mole fraction of Ethyl Oleate (X_1)



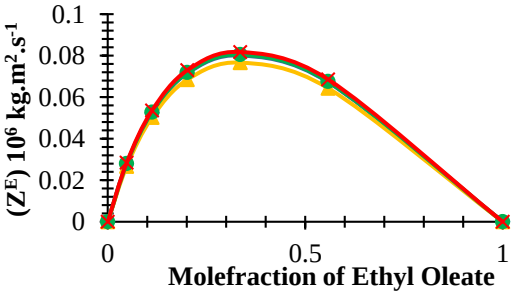
Graph 15 Excess Velocity Vs Mole fraction of Ethyl Oleate (X_1)



Graph 16 Deviation in Adiabatic Compressibility Vs Mole fraction of Ethyl Oleate (X_1)



Graph 17 Excess Intermolecular Free Length Vs Mole fraction of Ethyl Oleate (X_1)



Graph 18 Excess Acoustic Impedance Vs Mole fraction of Ethyl Oleate(X_1)

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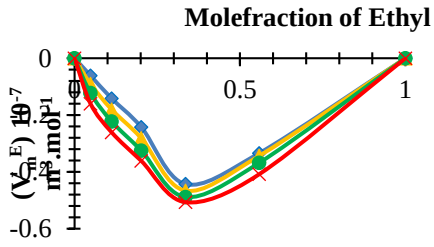
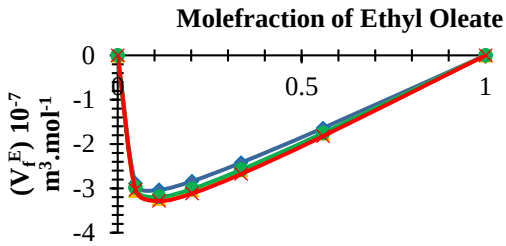
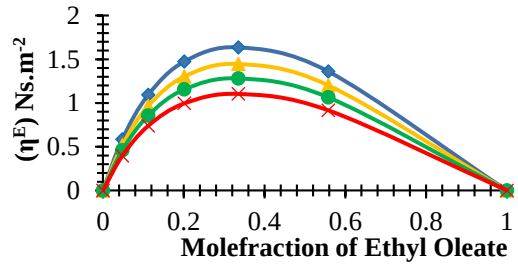


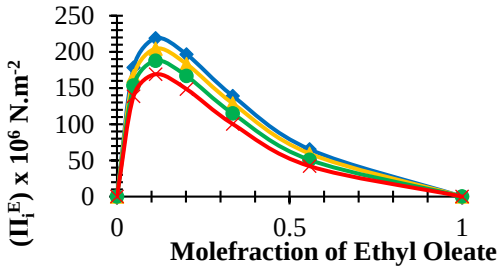
graph 19 Excess Molar Volume Vs Mole fraction of Ethyl Oleate (X_1)



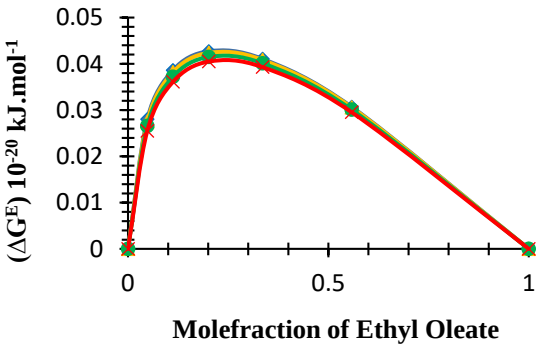
Graph 20 Excess Free Volume Vs Mole fraction of Ethyl Oleate (X_1)



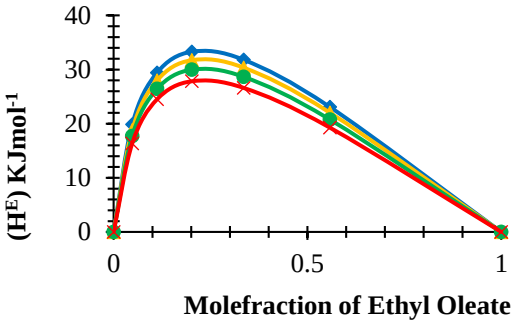
Graph 21 Deviation in Viscosity Vs Mole fraction of Ethyl Oleate (X_1)



Graph.22 Excess int. Pressure Vs Mole fraction of Ethyl Oleate (X_1)



Graph 23 Excess Gibb's Free Energy Vs Mole fraction of Ethyl Oleate(X_1)



Graph 24 Excess Enthalpy Vs Mole fraction of Ethyl Oleate (X_1)

In the above system the experimental values are changing gradually from values of selected organic compounds Ethyl Methyl ketone at X_1 is 0.0000 to the values of Ethyl Oleate at X_1 is 1.0000. In addition to the shape, size and dipole moment of the molecule the main contributions to the excess properties to the mixture of liquids are i. physical like weak Vander-Waal type, ii. Chemical like strong hydrogen bonding and iii. Structural like interstitial accommodation [8-9]. The experimental values of the velocity (U), density (ρ) and viscosity (η) decreases with increase in temperature and increases with increase in mole fraction of Ethyl Oleate at constant temperature. The derived parameters adiabatic compressibility (β_{ad}), intermolecular free length (L_f), molar volume (V_m)are increases with increase in temperature and there is no considerable change in the values of Rao's constant (R) and Wada's constant (W). The thermodynamic parameters free volume and Gibbs energy are increases with increase in temperature and acoustic impedance, internal pressure, enthalpy and relaxation time are decreasing with the increase in temperature as shown in Table 4. Except internal pressure all other parameters shown in the same table are increasing with the increase in mole fraction of Ethyl Oleate at given temperature.

The excess parameters explain the nature and strength of molecular interactions shown in Table 5. The excess velocity (U^E), deviation in adiabatic compressibility ($\Delta\beta_{ad}$), excess inter molecular free length (L_f^E), excess acoustic impedance (Z^E), excess molar volume ($V_m{}^E$) excess free volume (V_f^E), deviation in viscosity ($\Delta\eta$), excess internal energy (Π^E) , excess Gibb's free energy (ΔG^E) and excess Enthalpy (H^E) are calculated and presented in this chapter. The excess values are zero for pure compounds. It has been reported [31] that excess values of the binary mixtures result from the contributions due to the physical, chemical, and structural characteristics of the component liquids. The physical contributions comprise of dispersion forces and non-specific physical (weak) interactions, which lead to positive $V_m{}^E$ and $\Delta\beta_{ad}$ values. The chemical contributions involve breaking up of the associates present in the pure liquids, resulting in positive $V_m{}^E$ and $\Delta\beta_{ad}$ values. These chemical contributions

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also involve specific interactions such as formation of H-bonding, charge transfer (donor–acceptor) complexes and strong dipole–dipole interactions between the component molecules of the mixture, resulting in negative V_m^E and $\Delta\beta_{ad}$ values. The structural contributions are due to the geometrical fitting (favorable/unfavorable) of the molecules of very different molecular sizes into each other's structures resulting in negative/positive excess values. In the present investigation, the excess adiabatic compressibility ($\Delta\beta_{ad}$), the excess free volume (V_f^E), excess free length (L_f^E) exhibit negative values over the entire range of composition at all temperatures studied clearly indicate the presence of strong interactions [32-41] between Ethyl Oleate and Ethyl Methyl Ketone. Further, the excess internal pressure (π^E) which is usually explained in terms of molecular interaction, whose negative excess values suggest that strong molecular interaction between the unlike molecules [40].The variation of experimental, derived thermo-acoustic and excess parameters with change in temperature and mole fraction of Ethyl Oleate are shown as graphs from graph.1 to 24.

The excess values those explain the nature of interactions for the system are shown in relevant Table 5 for mixtures of Ethyl Oleate with Ethyl Methyl Ketone. The excess values are zero for pure liquids. The negative excess values indicate the strong interaction whereas the positive shows the relatively weak interactions [42-44]. Positive values of excess velocity and excess viscosity represent strong interactions. Except the excess velocity (UE), excess acoustic impedance (ZE), excess viscosity ($\Delta\eta$), excess Gibb's free energy (ΔGE) and excess Enthalpy (HE) remaining all the excess parameters for the binary mixture for the system is negative.

Conclusions

The ultrasonic velocity, density and viscosity measurements have been carried out for determination of ultrasonic parameters for the different composition range of Ethyl Oleate and Ethyl Methyl Ketone at different temperatures *viz*. 303.15 K, 308.15K, 313.15K and 318.15K.The negative values of $\Delta\beta_{ad}$ suggest that the binary liquid mixture is less compressible than the corresponding ideal liquids and the positive values indicate the reverse actions. The maximum negative values of adiabatic compressibility ($\Delta\beta_{ad}$) are -1.1584, -1.1670, -1.3522 and -1.4837 at the four temperatures under study. The negative excess values of molar volume (V_m^E) and positive excess values of viscosity ($\Delta\eta$) shows the molecular interaction between Ethyl Oleate and Ethyl Methyl Ketone due to dipole-dipole molecular interaction.

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