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Ultrasonic Studies of Binary Mixture Ethyl Oleate and Toluene in the temperature range of 303.15K to 318.15k.

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ABSTRACT

Ultrasonic velocity, density and viscosity for binary liquid mixture of fatty acid ester Ethyl Oleate with toluene have been measured at 2 MHz ultrasonic frequency within the temperature range of 303.15K to 318.15k. Thermo-acoustic parameters like adiabatic compressibility, acoustic impedance and intermolecular free length are calculated. The results are interpreted for interaction studies among the molecules of the mixtures.

Introduction

Ethyl Oleate is an organic compound with molecular formula $C_{20}H_{38}O_2$ which is a fatty acid ester formed by the condensation of oleic acid and ethanol. It is a colorless to light yellow liquid. Ethyl Oleate is produced by the body during ethanol intoxication [1].Toluene is colorless, water insoluble liquid with the smell associated with paint thinner. It is a mono substituted benzene derivative. It consists of a $-CH_3$ group attached to a phenyl group. Its IUPAC systematic name is methylbenzene. It is an aromatic hydrocarbon. Its polarity index is 2.4 and dielectric constant is 2.38. It is non polar solvent; - CH_3 group is electron donating group.

Velocity of sound waves in a medium is fundamentally related to the binding forces between the atoms or the molecules. Variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components [2–4] as well as strongly interacting components [5–7]. In the present study, ultrasonic Velocity (U), Viscosity (η) and density (ρ), of binary mixture of Ethyl Oleate and Toluene has been calculated and used to determine the acoustic parameters, adiabatic compressibility (β_{ad}) acoustic impedance (Z) and intermolecular free length (L_f) in order to explain the intermolecular interactions in these mixtures [2].FTIR spectra is utilized for confirmation of the expected interaction for the corresponding frequency peaks [22].

Materials and Experiments

All the materials procured are of Sigma-Aldrich AR grade and glassware used of Borosilicate make. Organic liquid Ethyl Oleate ($C_{20}H_{38}O_2$, 310.51g/mol), Toluene(C_7 H_8, 92.14gm/mol) of AR grade were procured from Sigma-Aldrich are used directly without purification. The densities and viscosities of the liquid compounds were measured with specific gravity bottle and Ostwald viscometer respectively pre calibrated with 3D [8] water of Millipore. 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 micrometer 0.001mm of Mittal Enterprises [9] was used for calculating velocities of sound waves and all the tests were conducted as per ASTM standard [10] procedures. FTIR Spectra were obtained with a Bruker ALPHA FT-IR spectrometer.

Theory and Calculations

In order to examine the inter molecular interactions in binary mixtures of Ethyl Oleate with Toluene, experiments were conducted to find the density, viscosity and velocity of 2MHz ultrasonic waves for pure liquids and for binary liquid mixtures under given temperature range. 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 Oleate for understanding inter and intra molecular interactions at each temperature. The derived and excess values are calculated by using the fallowing formulae for adiabatic compressibility (β_{ad}), Intermolecular free length (L_f) and 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

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

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 Where k is a constant, which is independent of temperature and its value is 4.28 X 109 for all liquids.

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Specific acoustic impedance (Z)

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

$Z = \rho U$

Excess thermodynamic parameters

With the help of excess acoustic 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

$Y^E = Y - (Y_1 X_1 + Y_2 X_2)$

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.

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

The difference of the adiabatic compressibility of the mixture and the sum of the fractional contributory adiabatic compressibilities of the two liquids is the deviation in adiabatic compressibility.

At a given mole fraction it is given by

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

Excess free length (L_f^E)

The excess free length can be calculated with formula $L_f^E = L_f - (L_{f1} X_1 + L_{f2} X_2)$

Excess acoustic impudence (Z^E) Excess acoustic impedance can be calculated by the relation

$Z^E = Z - (Z_1 X_1 + Z_2 X_2)$

Table 1. 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/m³	863.50	863.20[20]	859.34	859.50[20]	855.62	855.80[20]	852.04	855.20[20]
Viscosity (η) Ns/m²	5.3101	5.3094[20]	4.7164	4.7156[20]	4.2163	4.7300[19] 4.2137[20]	3.7820	3.7876[20]
Velocity (U) m/s	1368.16	1360.67[21]	1340.78	1342.98[21]	1324.00	1325.49[21]	1305.09	1308.17[21]

Table 2. Experimental and literature values of density (ρ), viscosity (η) and velocity (U) of 2MHz ultrasonic wave for pure Toluene

Parameter	303.15K		308.15K		313.15K		318.15K	
	Expt.	Lite.	Expt.	Lite.	Expt.	Lite.	Expt.	Lite.
Density(ρ) kg/m³	857.25	857.70[11] 857.30[14] 857.53[15]	851.59	852.60[14]	847.90	847.90[14] 848.14[15]	840.20	840.28[11]
Viscosity(η) Ns/m²	0.5765	0.5170[9] 0.5314[16] 0.5204[13] 0.5240[14] 0.5200[15]	0.5239	0.5083[16] 0.5068[11] 0.4980[24]	0.4983	0.4833[16] 0.4662[11] 0.4750[14]	0.4755	0,4630[16] 0.4379[11] 0.4379[12]
Velocity(U) m/s	1266.2	1283.7[15]	1255.6	-	1243.5	1241.1[15]	1222.2	1221.0[12]

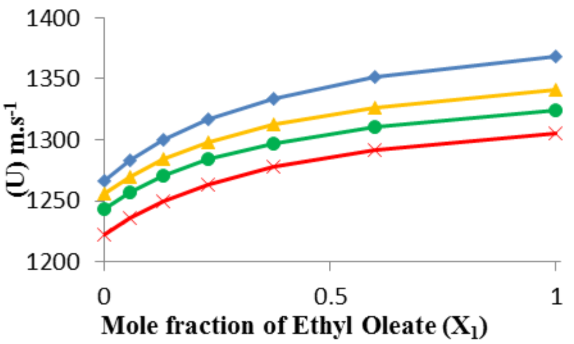
Table 3. Ultrasonic velocity (U), Density (ρ), Viscosity (η), adiabatic compressibility (β_{ad}), inter molecular free length (L_f), molar volume (V_m) ,Freee volume (V_f), acoustic impedance (Z)

Mole fraction (X_1)	Mole fraction (X_2)	Velocity m/sec (U)	Density Kg/m^3 (ρ)	Viscosity Nsm^{-2} (η)	Ad. Comp. 10^{-10} $N^{-1}.m^2$ (β_{ad})	Int. Mol. Free length 10^{-10} m (L_f)	Mol. Vol. (V_m)	Free Volume (V_f)	Acoustic Impedance (Z)
T=303.15 K									
0.0000	1.0000	1266.2	857.25	0.5765	7.2759	5.5971	107.48	3.2502	1.0854
0.0564	0.9436	1283.2	858.90	1.3655	7.0709	5.5177	121.62	1.098	1.1021
0.1300	0.8700	1300.2	859.30	2.1545	6.8841	5.4443	140.27	0.7004	1.1172
0.2301	0.7699	1317.2	860.70	2.9435	6.6968	5.3697	165.44	0.5742	1.1337
0.3741	0.6259	1334.2	861.10	3.7325	6.5242	5.3001	201.88	0.553	1.1488
0.5991	0.4009	1351.2	862.50	4.5215	6.3509	5.2292	258.52	0.614	1.1654
1.0000	0.0000	1368.1	863.49	5.3065	6.187	5.1613	359.61	0.8087	1.1814
T=308.15K									
0.0000	1.0000	1255.6	851.59	0.5239	7.448	5.7175	108.2	3.7049	1.0693
0.0564	0.9436	1269.8	853.55	1.2229	7.2657	5.6471	122.4	1.2757	1.0839
0.1300	0.8700	1284	854.2	1.9219	7.1006	5.5825	141.16	0.8163	1.0968
0.2301	0.7699	1298.2	855.8	2.6209	6.9333	5.5164	166.47	0.6692	1.111
0.3741	0.6259	1312.4	856.5	3.3199	6.7786	5.4545	203.08	0.6437	1.1241
0.5991	0.4009	1326.6	858.1	4.0189	6.622	5.3911	259.96	0.7133	1.1383
1.0000	0.0000	1340.8	859.33	4.7179	6.4733	5.3302	361.35	0.9359	1.1522
T=313.15K									
0.0000	1.0000	1243.5	847.9	0.4983	7.6272	5.8411	108.67	3.9363	1.0544
0.0564	0.9436	1256.9	849.9	1.1183	7.4474	5.7718	122.93	1.4367	1.0683
0.1300	0.8700	1270.4	850.6	1.7383	7.2846	5.7084	141.76	0.9339	1.0806
0.2301	0.7699	1283.8	852.2	2.3583	7.1195	5.6433	167.17	0.7711	1.0941
0.3741	0.6259	1297.3	852.9	2.9783	6.967	5.5826	203.94	0.7445	1.1064
0.5991	0.4009	1310.7	854.45	3.5983	6.8125	5.5203	261.07	0.8269	1.1199
1.0000	0.0000	1324.1	855.64	4.2183	6.6656	5.4605	362.91	1.0865	1.133
T=318.15K									
0.0000	1.0000	1222.2	840.28	0.4755	7.9669	6.0262	109.65	4.1147	1.027
0.0564	0.9436	1236	843.05	1.0265	7.7641	5.949	124	1.5944	1.042
0.1300	0.8700	1249.9	844.4	1.5775	7.581	5.8784	142.94	1.0558	1.0554
0.2301	0.7699	1263.7	846.7	2.1285	7.3959	5.8062	168.48	0.8799	1.07
0.3741	0.6259	1277.5	848.1	2.6795	7.2247	5.7386	205.38	0.8544	1.0835
0.5991	0.4009	1291.4	850.3	3.2305	7.0524	5.6698	262.64	0.9522	1.098
1.0000	0.0000	1305.2	852.1	3.7815	6.8892	5.6038	364.42	1.2526	1.1121

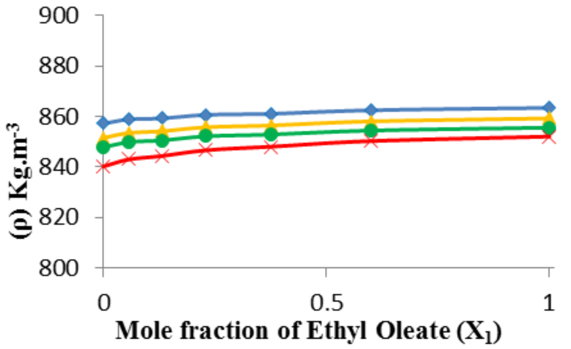
Table 4. Excess velocity(U^E), excess adiabatic compressibility($\Delta\beta_{ad}$), excess inter molecular free length(L_f^E), excess impedance(Z^E), excess molar volume(V_m^E),excess free volume(V_f^E),excess viscosity(Δη).

(X_1)	U^E	$\Delta\beta_{ad}$	L_f^E	Z^E	V_m^E	V_f^E	Δη
T=303.15 K							
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0564	11.24	-0.1436	-0.0548	0.01127	-0.0864	-2.0145	0.5222
0.1300	20.726	-0.2502	-0.0961	0.01932	0.0049	-2.2324	0.963
0.2301	27.513	-0.3286	-0.1271	0.02616	-0.0635	-2.1142	1.2786
0.3741	29.821	-0.3443	-0.134	0.02751	0.0726	-1.7838	1.3864
0.5991	23.877	-0.2727	-0.1068	0.02245	-0.015	-1.1735	1.1112
1.0000	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	0.0000	0.0000	0.0000
0.0564	9.3795	-0.1272	-0.0485	0.00989	-0.0962	-2.2727	0.462
0.1300	17.293	-0.2204	-0.0845	0.01673	-0.005	-2.5281	0.8519
0.2301	22.951	-0.2901	-0.1119	0.02262	-0.0662	-2.3976	1.1306
0.3741	24.871	-0.3043	-0.1179	0.02374	0.0592	-2.0241	1.2251
0.5991	19.905	-0.2416	-0.0942	0.01937	-0.0182	-1.3315	0.9805
1.0000	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
0.0564	8.8836	-0.1255	-0.0478	0.00947	-0.1028	-2.3386	0.4098
0.1300	16.379	-0.2173	-0.0831	0.01598	-0.02	-2.6313	0.7556

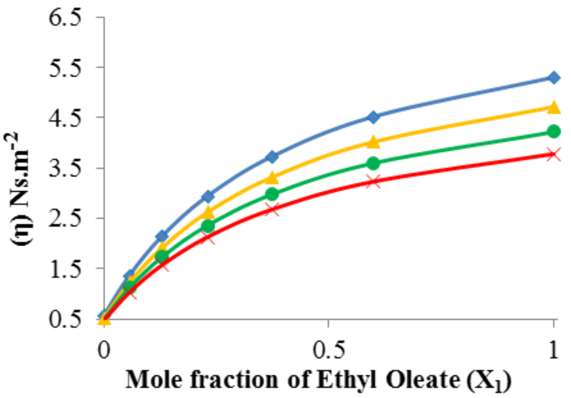
0.2301	21.738	-0.2861	-0.11	0.02159	-0.0844	-2.5085	1.0028
0.3741	23.556	-0.3	-0.1159	0.02262	0.0382	-2.1244	1.0866
0.5991	18.852	-0.2382	-0.0926	0.01843	-0.0306	-1.4008	0.8697
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T=318.15 K							
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0564	9.1197	-0.1417	-0.0532	0.01021	-0.1178	-2.3579	0.3633
0.1300	16.808	-0.245	-0.0925	0.01726	-0.0305	-2.6847	0.6697
0.2301	22.297	-0.3218	-0.1223	0.02328	-0.1015	-2.5728	0.8883
0.3741	24.144	-0.3374	-0.1289	0.02448	0.0145	-2.185	0.9619
0.5991	19.302	-0.2671	-0.1027	0.01989	-0.0525	-1.4432	0.769
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000



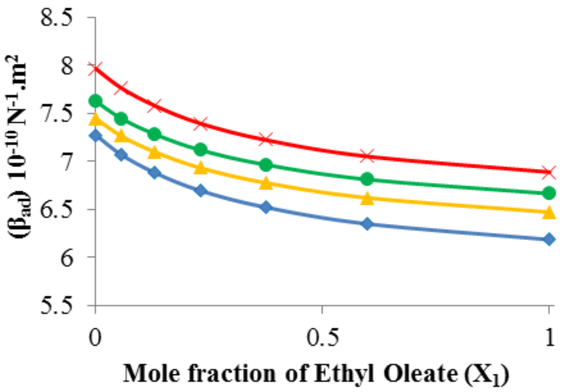
Graph 1. Ultrasonic Velocity Vs Mole fraction of Ethyl Oleate (X_1)



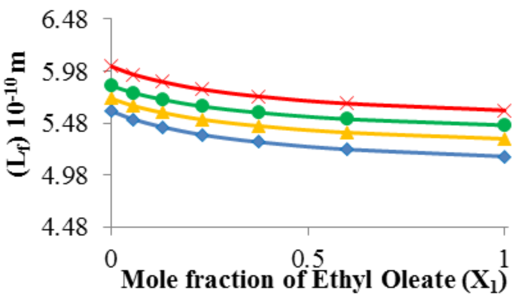
Graph 2. DensityVs Mole fraction of Ethyl Oleate (X_1)



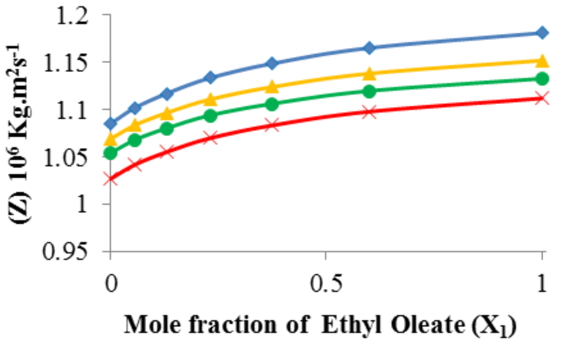
Graph 3. ViscocityVs Mole fraction of Ethyl Oleate (X_1)



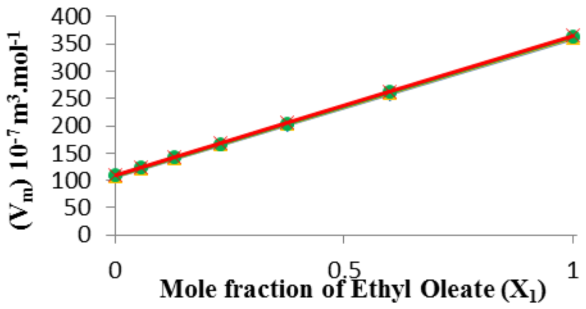
Graph 4. Adiabatic Compressibility Vs Mole fraction of Ethyl Oleate(X_1)



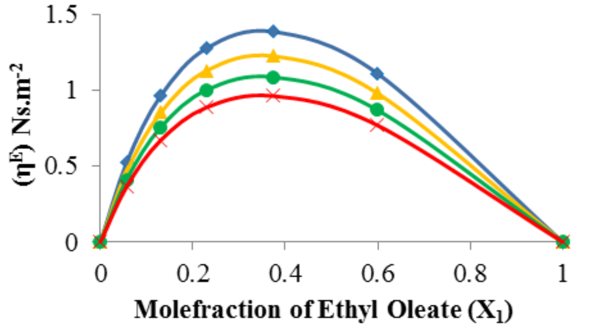
Graph 5. Intermolecular Free Length Vs Mole fraction of Ethyl Oleate(X_1)



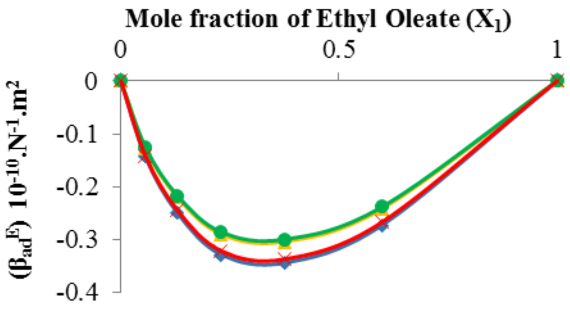
Graph 6. Acoustic Impedance Vs Mole fraction of Ethyl Oleate(X_1)



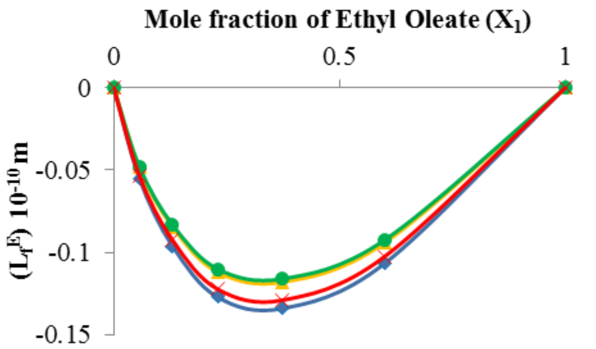
Graph 7. Molar Volume Vs Mole fraction of Ethyl Oleate(X_1)



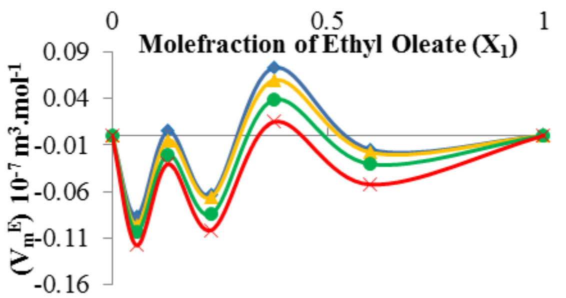
Graph 8. Deviation in Viscosity Vs Mole fraction of Ethyl Oleate(X_1)



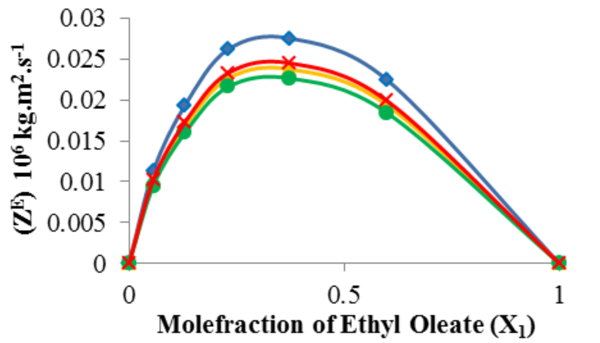
Graph 9. Excessadia. Compressibility VsMolefraction of Ethyl Oleate(X_1)



Graph 10. Excess Intermolecular Free Length Vs Mole fraction of Ethyl Oleate(X_1)



Graph 11. Excess Molar Volume Vs Mole fraction of Ethyl Oleate(X_1)



Graph 12. Excess Acoustic Impedance Vs Mole fraction of Ethyl Oleate(X_1)

303.15 K 308.15 K 313.15 K 318.15 K

There is a characteristic absorption at 1737 cm^{-1}, which is attributed to the stretching frequency of the C=O bond of the ester. The band at 3086cm^{-1} referred to the stretching frequencies of aromatic ═C-H bond. The strong bands at 724 and 691 cm^{-1}confirmed that the aromatic ring having mono substitution.

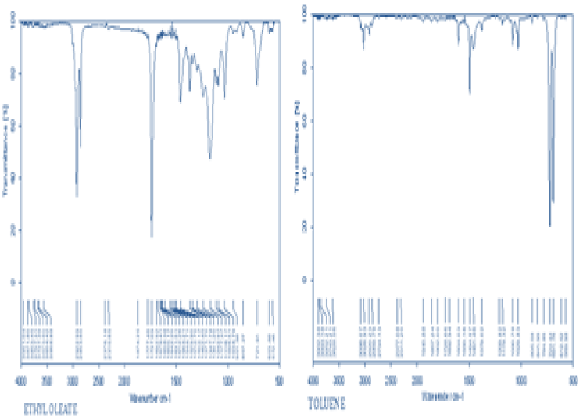


Chart 1. FTIR spectrum of pure Ethyl Oleate and pure Toluene

The absorption band at 1736cm^{-1}, which is attributed to the stretching frequency of the C=O bond of the ester. The band at 2923cm^{-1} referred to the stretching frequencies of aromatic ═C-H bond. The strong bands at 727 and 693 cm^{-1} confirmed that the aromatic ring having mono substitution[22].

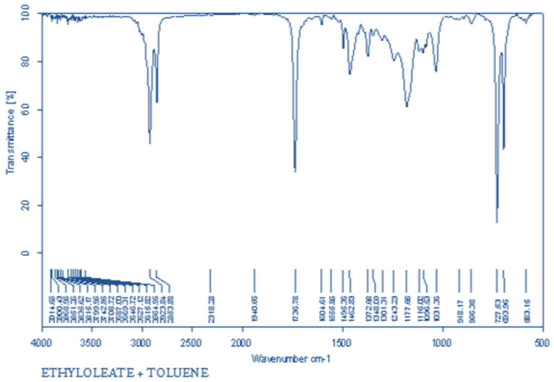


Chart 2. FTIR spectrum of Ethyl Oleate + Toluene

Results and Discussion

Values of density (ρ), ultrasonic velocity (U), viscosity (η), adiabatic compressibility (β_{ad}), intermolecular free length (L_f), and acoustic impedance (Z) along with mole fraction of Ethyl Oleate in toluene are listed in the “table.3”. The excess parameter of adiabatic compressibility, intermolecular free length, and acoustic impedance along with mole fraction of Ethyl Oleate in toluene listed in “table.4”. Also the graphical representation for above said parameter against mole fraction (X) of Ethyl Oleate is depicted in figures. Ultrasonic velocity in medium is depends upon binding forces between the molecules. From the “table 3” it is clear that in the system toluene + Ethyl Oleate the ultrasonic velocity decreases with increasing mole fractions of Ethyl Oleate. The decrease in velocity and increase in compressibility were attributed to the formation of hydrogen bonds between solute and solvent molecules [17]. From “table 4”, the negative values of excess acoustic impedance, shows there are weak molecular interactions existing between unlike molecules. [18] Most of values of excess intermolecular free lengths are negative. It shows sound waves cover long distance due to decrease in intermolecular free length. Values of excess adiabatic compressibility shows that weak molecular interaction between unlike molecules of components liquid.

Conclusions

The ultrasonic velocity, density, viscosity and other related experimental, derived and their excess parameters were calculated. The miscible organic binary liquid mixture of Ethyl Oleate and toluene shows the negative excess free volume (V_f^E),excess adiabatic compressibility (β_{ad}), and positive excess viscosity (Δη)represent the strong interaction between the unlike molecules of the binary mixture.

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