Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(2):281-285
(http://derpharmachemica.com/archive.html)

Study of molecular interactions among ester and m-toluidine using ultrasonic technique

M. Srilatha[a], D. Chinnarao[a], G. V. Gaurav[b], G. Hima Bindu[a], K. Raja[a], B. Venkateswara Rao[a] and Ch. V. Padmarao[a]*

[a]*Dept. of Engg. Chemistry, Andhra University College of Engineering (A), Visakhapatnam (India)*
[b]*Dept. of Engg. Chemistry, GVP college for degree and PG courses, School of Engineering, Rushikonda, Visakhapatnam (India)*

ABSTRACT

The molecular interactions of Ethyl Oleate with m-Toluidine were studied using ultrasonic velocity, density and viscosity measurements at 303.15, 308.15, 313.15 and 318.15K. From the experimental data, the acoustical parameters such as adiabatic compressibility (β_{ad}), free length (L_f), free volume (V_f), acoustic impedance (Z) and their excess values were estimated using standard relation. The results of these parameters are attributed to weak hydrogen bond between solute and solvent molecules. The intermolecular interactions and structural effects are analyzed on the basis of the measured and derived properties.

Keywords: Ultrasonic study; binary mixture; acoustical parameters; molecular interaction.

INTRODUCTION

In the estimation of structural properties of molecules, the study of molecular interaction in liquid mixtures is of considerable importance. Ester is one of the best candidates that exist as dipolar associates in their pure liquid state and find wide industrial applications [1]. It is used as solvents, essences and perfumes and they play an important role as flavoring agents in many chemical formulations. Therefore, interesting results may be obtained regarding molecular interactions between unlike molecules in the binary mixture. The measurement of ultrasonic speed enables the accurate determination of some useful parameters and their excess functions, which are highly sensitive to molecular interactions and can be used to provide qualitative information about the physical nature and strength of molecular interaction in the liquid mixtures. Ultrasonic velocity studies in conjunction with density and viscosity studies also play a vital role in the investigation of intermolecular interaction in mixed liquid systems. The results were analyzed in terms of intermolecular interactions between the constituent components of the mixture.

MATERIALS AND METHODS

All the materials procured of Sigma-Aldrich AR grade and glassware used of Borosilicate make. Organic liquid Ethyl Oleate ($C_{20}H_{38}O_2$, 310.51g/mol), m-Toluidine 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 pre calibrated with 3D [2] water of 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 micrometer 0.001mm of Mittal Enterprises [3] was used for calculating velocities of sound waves and all the tests were conducted as per ASTM standard [4] procedures.

5. Theory and Calculations

The acoustical parameters are calculated from U, ρ, and η [5-8] using following relation.

a). Ultrasonic Velocity (U)

The relation used to determine the ultrasonic velocity is given by,

$$\mathbf{U = f\lambda\ ms^{-1}}$$

Where, f - Frequency of ultrasonic waves λ - Wave length

b). Adiabatic compressibility (β_{ad})

The intermolecular association or dissociation leads to structural arrangement of the constituent particles. This structural change of the molecule takes place due to the existence of electrostatic field between interacting molecules may affect the adiabatic compressibility which is defined as

$$\mathbf{\beta_{ad} = (1/U^2\rho)\ kg^{-1}\ ms^2}$$

Where U – Ultrasonic velocity ρ – Density of the solution.

c). Internal pressure (π_i)

On the basis of statistical thermodynamics, Surya narayana derived an expression for the determination of internal pressure through use of concept of free volume

$$\mathbf{\pi_i = bRT\ (\beta_{ad}\eta/U)^{1/2}\ (\rho^{2/3}/M_{eff})^{7/6}}$$

Where T – Absolute temperature, ρ - Density, and R is the gas constant, M_{eff} – effective molecular weight.

d). Free Length (L_f)

Jacobson introduced the concept of the free length in liquids. He suggested the following relation to calculate the intermolecular free length.

$$\mathbf{L_f = (K/U\ \rho^{1/2})\ m}$$

Where U – Ultrasonic velocity of liquid, ρ – Density of liquid, K – Jacobson temperature dependent constant defined as

$$\mathbf{K = (93.875 + 0.345T)\ X\ 10^{-8}}$$

e). Acoustic impedance (Z)

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

$$\mathbf{Z = U\rho}$$

f). Free volume (V_f)

The ultrasonic velocity and effective molecular weight are influenced by the free volume (V_f), which is given by the relation

$$\mathbf{V_f = [\ M_{eff}\ U/\ K\eta]^{3/2}}$$

RESULTS AND DISCUSSION

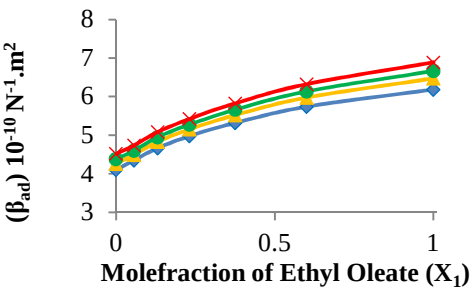
Table.1: Ultrasonic velocity (U), Density (ρ), Viscosity (η), adiabatic compressibility (β_{ad}), inter molecular free length (L_f), free volume (V_f), Acoustic impedance

Mole fraction (X_1)	Velocity (U) m/sec	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)	Free Volume (V_f)	Acoustic Impedance (Z)
T=303.15 K							
0.0000	1569.9	989.8	2.7415	4.0993	4.2012	0.5427	1.5539
0.0567	1536.3	972.9	3.1694	4.355	4.3302	0.4928	1.4947
0.1308	1502.7	948.9	3.5973	4.6671	4.4827	0.4716	1.4259
0.2313	1469.1	930.7	4.0252	4.9786	4.6299	0.4767	1.3673
0.3758	1435.5	899.4	4.4531	5.3959	4.8200	0.5140	1.2911
0.6008	1401.9	886.5	4.8810	5.7401	4.9714	0.6036	1.2427
1.0000	1368.2	863.5	5.3089	6.186	5.1609	0.8083	1.1815
T=308.15 K							
0.0000	1547.3	979.8	2.5290	4.2629	4.3255	0.5993	1.516
0.0567	1512.89	971.8	2.8935	4.4958	4.4421	0.5525	1.4702
0.1308	1478.48	946.5	3.2580	4.8333	4.6058	0.5347	1.3994
0.2313	1444.07	930.1	3.6225	5.1557	4.7570	0.5452	1.3431
0.3758	1409.66	894.2	3.9870	5.6277	4.9700	0.5916	1.2605
0.6008	1375.25	884.7	4.3515	5.9764	5.1216	0.6979	1.2167
1.0000	1340.84	859.3	4.716	6.4729	5.3301	0.9365	1.1522
T=313.15 K							
0.0000	1532.1	972.1	2.2762	4.3824	4.42759	0.6916	1.4894
0.0567	1497.44	969.1	2.5995	4.6018	4.53708	0.6392	1.4512
0.1308	1462.78	943.8	2.9228	4.9517	4.70643	0.6198	1.3806
0.2313	1428.12	929.1	3.2461	5.2772	4.85864	0.6329	1.3269
0.3758	1393.46	892.1	3.5694	5.7729	5.0817	0.6874	1.2431
0.6008	1358.8	882.7	3.8927	6.1358	5.2390	0.811	1.1994
1.0000	1324.14	855.6	4.2160	6.6659	5.46061	1.0873	1.1329
T=318.15 K							
0.0000	1515.6	965.3	2.1218	4.5099	4.534	0.7561	1.463
0.0567	1480.5	964.2	2.3985	4.7316	4.6441	0.7093	1.4275
0.1308	1445.4	941.3	2.6752	5.0848	4.8143	0.6958	1.3606
0.2313	1410.4	927.3	2.9519	5.4215	4.9712	0.717	1.3078
0.3758	1375.3	890.5	3.2286	5.9372	5.2022	0.7843	1.2247
0.6008	1340.2	881.2	3.5053	6.3181	5.3665	0.9305	1.1810
1.0000	1305.1	852.1	3.782	6.8898	5.6041	1.2523	1.1121

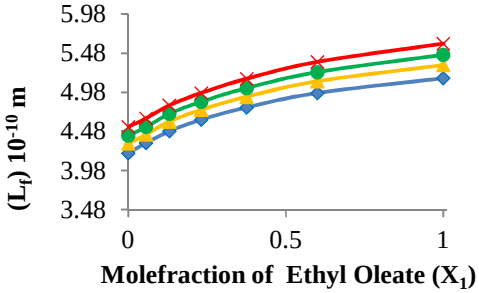
The experimental values of density, viscosity and ultrasonic velocity for the system at 303.15, 308.15, 313.15 and 318.15K are presented in Table 1.The values of adiabatic compressibility, free length, free volume the internal pressure and acoustic impedance for the mixture at three different temperatures are given in Table 1. The respective excess values of these parameters have been evaluated and presented in Table 3. The graphs 1-4 represented the variations in adiabatic compressibility (β), free length (L_f), free volume (V_f), acoustic impedance (Z) with increasing mole fraction of Ethyl Oleate and the graphs 5-8 represents the their excess values with increasing mole fraction of Ethyl Oleate. The density and ultrasonic velocity decrease with increase in concentration of Ethyl Oleate (aliphatic ester).This behavior is different from the ideal mixture behavior and this can be attributed to the intermolecular interaction in the systems [9-11]. However, the density and velocity decrease with increase in temperature indicates the decrease in intermolecular force due to increase in thermal energy of the system which causes a volume expansion and hence an increase in free length. When compared with aliphatic ester, the aromatic ester has higher values of velocity. The interactions between the molecules of m-Toluidine with Ethyl Oleate are found to be stronger. As stated earlier, the molecules of m-Toluidine are self associated through hydrogen bonding of their amino group (N-H) and ester molecules are polar group C=O, thus the mixing of m-Toluidine molecules with Ethyl Oleate molecules forming new H-bond (N–H ----- O=C) between hydrogen atom of m-Toluidine and oxygen atom of Ethyl Oleate. This contributes to an increase in free length and adiabatic compressibility. The regular increase in free length is due to the loose packing of the molecules inside the shield, which may be brought by weakening of molecular interaction.

Table.2: Excess adiabatic compressibility ($\Delta\beta_{ad}$), excess inter molecular free length (L_f^E), excess Impedance (Z^E), excess free volume (V_f^E)

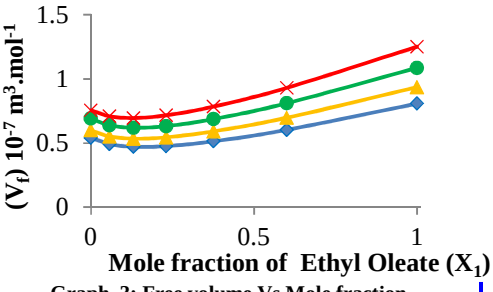
Mole fraction (X_1)	Excess Ad. Comp. $\Delta\beta_{ad}$	Excess Int. Mol. Free length L_f^E	Excess Acoustic Impedance Z^E	Excess Free Volume V_f^E
T=303.15 K				
0.0000	0.0000	0.0000	0.0000	0.0000
0.0567	0.1372	0.0745	-0.0381	-0.065
0.1308	0.2948	0.156	-0.0793	-0.1059
0.2313	0.3964	0.2066	-0.1004	-0.1274
0.3758	0.5124	0.2582	-0.1229	-0.1285
0.6008	0.387	0.1936	-0.0874	-0.0987
1.0000	0.0000	0.0000	0.0000	0.0000
T=308.15 K				
0.0000	0.0000	0.0000	0.0000	0.0000
0.0567	0.1067	0.0592	-0.0251	-0.0661
0.1308	0.2799	0.1483	-0.0688	-0.109
0.2313	0.3793	0.198	-0.0884	-0.1325
0.3758	0.5314	0.2656	-0.1183	-0.1349
0.6008	0.3827	0.1912	-0.0803	-0.1045
1.0000	0.0000	0.0000	0.0000	0.0000
T=313.15 K				
0.0000	0.0000	0.0000	0.0000	0.0000
0.0567	0.0886	0.0503	-0.0178	-0.0751
0.1308	0.2683	0.1426	-0.0618	-0.1239
0.2313	0.3628	0.1904	-0.0795	-0.1509
0.3758	0.5276	0.2637	-0.1116	-0.1538
0.6008	0.3765	0.1885	-0.075	-0.1192
1.0000	0.0000	0.0000	0.0000	0.0000
T=318.15 K				
0.0000	0.0000	0.0000	0.0000	0.0000
0.0567	0.0849	0.0486	-0.0153	-0.0753
0.1308	0.2602	0.1389	-0.056	-0.1258
0.2313	0.3558	0.1873	-0.0732	-0.1549
0.3758	0.5262	0.2631	-0.1055	-0.1596
0.6008	0.3715	0.1865	-0.0702	-0.1251
1.0000	0.0000	0.0000	0.0000	0.0000



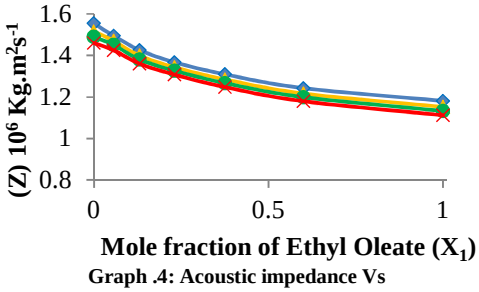
Graph .1: Add. Compressibility Vs Mole fraction of Ethyl Oleate(X_1)



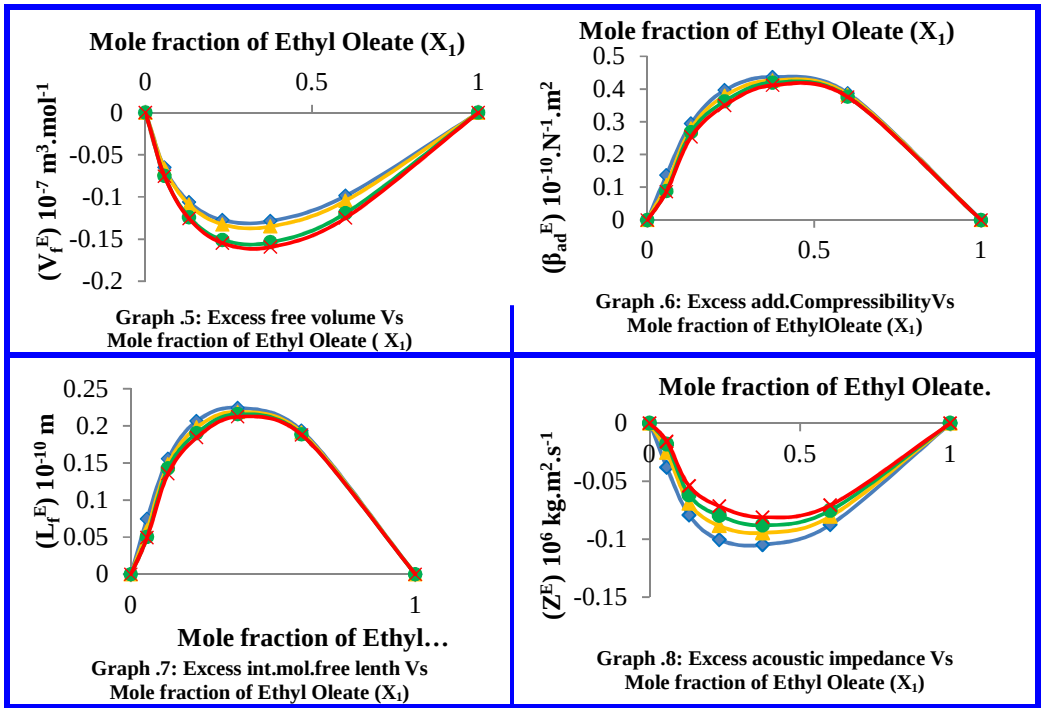
Graph .2: Int.mol. Free Length Vs Mole fraction of Ethyl Oleate (X_1)



Graph .3: Free volume Vs Mole fraction of Ethyl Oleate (X_1)



Graph .4: Acoustic impedance Vs Mole fraction of Ethyl Oleate (X_1)



Graph .5: Excess free volume Vs Mole fraction of Ethyl Oleate (X_1)

Graph .6: Excess add.CompressibilityVs Mole fraction of EthylOleate (X_1)

Graph .7: Excess int.mol.free lenth Vs Mole fraction of Ethyl Oleate (X_1)

Graph .8: Excess acoustic impedance Vs Mole fraction of Ethyl Oleate (X_1)

CONCLUSION

The ultrasonic velocity, density and viscosity measurement, the experimental data, the acoustical parameters such as adiabatic compressibility (β_{ad}), free length (L_f), free volume (V_f), acoustic impedance (Z) and their excess values were calculated using standard relation at 303.15 to 318.15K. The results of these parameters are attributed to weak hydrogen bond between solute and solvent molecules.

Acknowledgments

The authors are very much grateful to Andhra University for providing infrastructure facilities. Also thankful to UGC for sanctioning fellowship which is financially helped for procuring instruments and chemicals.

REFERENCES

[1] Wankhede, H.N, Wankhede, D.S, Lande, M.K. and Arbad, B.R.J. *Chem. Thermodyn*. 38 (**2006**),1664.
[2] Joseph Kestin, MordechaiSokolov, Willium A. Wakeham. *J. Phys. Chem. Ref. Data*, **1978**, 7(3), 941.
[3] Instruction manuals for ultrasonic interferometer model F-05, constant temperature water bath Mittal Enterprises.
[4] 4. American Society for Testing and Materials (ASTM) Standard D6751. ASTM: West Conshohocken, PA, **2009**.
[5] PS Nikam; TR Mahale; M Hasan. *J.Acoustica Acta.*,**1998**, 84, 579.
[6] PS Nikam; MC Jadhav; MJ Hasan. *J. Mol Liq.*, **1998**, 76, 1.
[7] PS Nikam; TR Mahale; M Hasan. *Indian J. Pure Appl Phys*.,**1999**, 37, 92.
[8] V Kannappan; R Jayasanthi; EJP Malar. *J.Phy Chem Liq*., **2000**, 40,133.
[9] Tiwari, K., Patra, C. and Chakravarthy, V., *Acoust. Lett*. 19, (**1995**) 53-57.
[10] Rita Mehra, Ashish Gupta, *J.Pure. Appl. Ultrason*. 23 (**2003**),130-135.
[11] Kannappan, AN. and Rajendran, V., *Ind.J. Pure & Appl. Phys*. 30 (**1992**) 240-242.