International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.7, pp 3181-3187, 2015

ICEWEST-2015 [05th - 06th Feb 2015]
International Conference on Energy, Water and Environmental Science & Technology
PG and Research Department of Chemistry, Presidency College (Autonomous), Chennai-600 005, India

Ultrasonic Studies on Ternary Liquid Mixtures at Different Temperatures

J.Senthil Murugan* & Dr.S.Chidambara Vinayagam

Post Graduate and Research Department of Chemistry, Presidency College, Chennai – 600 005.

Abstract: The Measurement of Ultrasonic Velocity, Density and Viscosity has been made for the ternary liquid mixture of Mesitylene + 1-Propanol + Cyclohexane at 303K, 308K and 313K. From these data, acoustical parameters such as adiabatic compressibility, free length, free volume, internal pressure, Absorption coefficient, viscous relaxation time, Available volume, cohesive Energy, Lenard Jones potential, free energy of activation, Molecular interaction parameter and formation constant have been evaluated using the standard relations. The results have been analyzed on the basis of variations in ultrasonic velocity and free lengths. The presence of weak interactions is noticed in the ternary system.
Keywords: Ultrasonic Studies, Ternary Liquid Mixtures.

Introduction:

The velocity of sound waves in a medium is fundamentally related to the binding forces between the atoms or the molecules. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components as well as strongly interacting components. A large number of studies have been made on the intermolecular interaction in the liquid system by various methods like ultraviolet, Dielectric constant, Infrared, Raman Effect, Nuclear magnetic resonance and Ultrasonic method. In recent years Ultrasonic method has become a powerful tool in providing information regarding the physico-chemical properties of liquid system[1-4]. The increase (or) decrease in Ultrasonic velocity have been used in understanding the nature of molecular interactions in the pure liquids of ternary mixtures. The variation of Ultrasonic velocity and Related parameters show much light upon structural changes associated with the liquid upon structural changes associated with the liquid mixtures having weakly interacting components as well as strongly interacting components. The study of liquid mixtures containing of polar and non-polar components find solutions that generally do not behave ideally.

In the present study Ultrasonic velocity, Density and viscosity were measured experimentally for the ternary system namely Mesitylene + 1-Propanol + Cyclohexane at different temperatures 303K, 308K and 313K and predicted the possible molecular interaction between the unlike molecules. The presence of $-CH_3$ group in Mesitylene implies that dipole – induced dipole interaction is weaker in higher hydrocarbons owing to its decrease polarisabilities with increase of $-CH_3$ group[5-15].

Materials and Methods:

The liquid mixtures of various concentrations were prepared by taking AR grade chemicals, which were purified by standard methods.

The Ultrasonic velocity in liquid mixtures have been measures using an ultrasonic interferometer (Mittal type: Model: F81) working at frequency 2 MHz with an overall accuracy of ± 0.1ms^{-1}. The density and viscosity are measure using a Pycknometer and an Ostwald's viscometer with an accuracy of ± 0.1 kg m^{-3} and 0.0001 m $Nm^{-2}s$, respectively. All the precautions were taken to minimize the possible experimental error. The set-up is checked for standard liquids.

The expression used to determine the Ultrasonic Velocity is $U = f \lambda\ ms^{-1}$ ---------- (1)
The densities of the mixture using the formula $\rho_2 = (w_2/W_1)\rho_1$---------- ----------(2)

where w_1 = weight of distilled water, w_2 = weight of experimental liquid, ρ_1 = Density of water, ρ_2 = Density of experimental liquid.

The viscosity was determined using the relation, $\eta_2 = \eta_1 (t_2/t_1) (\rho_2/\rho_1)$----------(3)

Using the measured data, the following acoustical parameters can be calculated.

Adiabatic compressibility (β)
$K = (1/U^2\rho)\ kg^{-1}ms^{-2}$ ----------(4)
Free Length (L_f)
$L_f = (K/U\rho^{1/2})$ m----------(5)

Where, K is Jacobson's constant. This constant is a temperature dependent whose value at any temperature (T) is given by $(93.875 + 0.3445T)\ X10^8$.

Acoustic Impedance (Z)
$Z = U \rho$ kg $m^{-2}s^{-1}$----------(6)
Free Volume (V_f)
$V_f = (M_{eff}\ U/k\eta)^{3/2}\ m^3$ ----------(7)

Where, M_{eff} is the effective molecular weight($M_{eff} = \sum m_i\ x_i$ in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents respectively and k is a temperature independent constant equal to $4.28\ X\ 10^9$ for all liquids.

Internal Pressure (π_i)

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

$\Pi_i = bRT\ (k\eta/U)^{1/2}\ (\rho^{2/3}/M_{eff})^{7/6}$--------(8)

Where T= is the absolute temperature ρ= is the density and R is the gas constant.

M_{eff} = is the effective molecular weight.
Absorption coefficient (α/f^2): It can be calculated from the viscosity using the relation,
$\alpha/f^2 = (8\pi^2\eta/3\rho U^3)\ Nps^2m^{-1}$----------(9)
Viscous Relaxation time (τ) It is calculated using the relation
$\tau = 4\eta/3\rho u^2)s$----------(10)
Available Volume (V_a): It can be calculated from Schaff's relation
$V_a = V_m\ (1-U/U_a)m^3$----------(11)
Where V_m is the molar volume and $U_a = 1600\ ms^{-1}$.
Cohesive Energy (CE): It is usually given as a product of internal pressure (π_i) and molar volume (V_m).
$CE = \pi_i\ V_m$ kj mol^{-1}
Free energy of Activation (ΔG^*) = $-K_B\ T\ ln\ (h/\tau K_B T)$ $kjmol^{-1}$----------(12)

Where K_B = Boltzman's constant ($1.3806X10^{-23}Jk^{-1}$) T = is the temperature h = is the Planck's constant ($6.626X10^{-34}Js$).

The Lenard Jones potential exponent Is given by LJP = $6V_m/V_a$ ----------(13)
V_m = the molar volume V_a = the available volume

Formation constant: To calculate the formation constant values of the charge transfer complexes, appreciable to weak complexes and in very dilute solutions. The stability constant is calculated using the relation

$K = Y/(b\text{-}y)^2$ dm^3 mol^{-1}----------(14) Where,
$Y = (a\text{-}k^{1/2}b)/k\text{-}k^{1/2})$; $k = x/y$
X = difference between U_{cal} and U_{obs} at lower concentration 'a',
Y = difference between U_{cal} and U_{obs} at higher concentration 'b' and
U_{cal} = the ultrasonic velocity of the mixture. This equation can be used to calculate stability constant values for different combination concentration 'a' and 'b'.

Result and Discussion:

The measured Ultrasonic velocity, Density and Viscosity at various equimolar concentration represented in Table 1.

Table:1 Values of Ultrasonic velocity, Density and Viscosity of the system: Mesitylene + 1-Propanol + Cyclohexane

Concentration	Ultrasonic Velocity m/sec			Density (ρ) kg/m			Viscosity (Ƞ)X10^{-4} Nsm^{-2}		
	Temperature (K)			Temperature (K)			Temperature (K)		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
1X10^{-3}	1204.6	1198.7	1184.6	725.4	730.3	736.3	6.954	7.115	7.174
2X10^{-3}	1217.2	1201.7	1175.6	721.7	728.4	732.4	6.918	6.982	7.021
3X10^{-3}	1201.2	1187.8	1171.0	724.4	735.2	737.8	6.830	6.932	6.957
4X10^{-3}	1208.2	1186.4	1165.7	728.3	730.7	733.4	6.867	6.890	6.915
5X10^{-3}	1190.4	1180.0	1153.6	724.6	725.6	730.2	6.946	6.956	7.000
6X10^{-3}	1208.6	1184.2	1154.5	725.2	726.4	732.1	6.838	6.963	7.018
7X10^{-3}	1210.1	1193.6	1158.1	719.6	717.3	729.3	6.898	6.989	7.106
8X10^{-3}	1206.1	1175.6	1155.3	722.7	732.6	735.3	6.814	7.138	7.164
9X10^{-3}	1199.8	1179.8	1150.8	727.3	728.4	736.4	6.972	7.097	7.175
10X10^{-3}	1216.2	1183.8	1179.1	725.2	726.3	732.6	6.952	7.076	7.138

Solvent: Cyclohexane

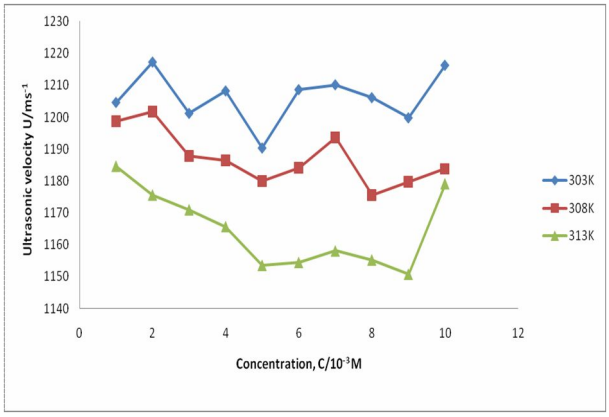

Fig 1. Plot of Ultrasonic Velocity Vs Concentration for Mesitylene and 1-proponal at Different Temperature

The variation of Ultrasonic velocity depends upon the increase (or) decrease of intermolecular free length after mixing the components. On the basis of a model for propagation proposed by Kincaid and Erying (1938). Ultrasonic Velocity should increase if the intermolecular free length decreases as a result of mixing the components and vice versa. This fact is observed in the present investigation. The dispersive type of interaction occur between the 1-propanol and Cyclohexane due to the non-polar nature of Cyclohexane and its inertness

towards electron donors. The increase in free length with increase of temperature is due to the loose packing of molecular inside the shield, which may be brought about by weakening of molecular interactions.

A decrease in free volume and a increase in internal pressure to the increase in magnitude of interaction. As the dipole moment of Cyclohexane is zero, the decrease in free volume shows that the clustering is not due to H-bonding but may be due to dispersive interactions. The calculated values of Adiabatic compressibility, Free Length, Free volume and Internal pressure are represented in Table2.

Table 2: Values of Adiabatic Compressibility (β), Free Length (L_f), Free Volume (V_f) & Internal pressure (π_i) of the system: Mesitylene + 1-Propanol + Cyclohexane

Concentration	Adiabatic compressibility			Free Length (pm)			Free Volume X $10^{-7}m^3$			Internal Pressure		
	Temperature (K)			Temperature (K)			Temperature (K)			Temperature (K)		
	303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K
$1X10^{-3}$	9.50	9.53	9.68	61.2	61.3	61.7	2.649	2.540	2.465	2875.58	2929.11	2974.81
$2X10^{-3}$	9.35	9.51	9.88	60.2	60.7	61.8	2.035	1.969	1.890	3555.12	3616.80	3679.77
$3X10^{-3}$	9.57	9.64	9.88	60.8	61.1	61.8	2.034	1.956	1.904	3564.79	3647.23	3688.46
$4X10^{-3}$	9.41	9.72	10.00	60.3	61.3	62.3	2.035	1.970	1.908	3576.87	3623.41	3671.24
$5X10^{-3}$	9.74	9.90	10.30	61.4	61.9	63.1	1.956	1.927	1.845	3611.85	3633.57	3702.12
$6X10^{-3}$	9.44	9.82	10.20	60.6	61.5	62.9	2.026	1.946	1.814	3558.50	3631.88	3711.97
$7X10^{-3}$	9.49	9.79	10.20	60.6	61.5	62.9	2.026	1.946	1.814	3553.50	3593.78	3719.80
$8X10^{-3}$	9.51	9.88	10.20	60.7	61.8	62.8	2.053	1.843	1.785	3547.94	3711.50	3760.11
$9X10^{-3}$	9.55	9.86	10.30	60.8	61.8	63.0	1.968	1.869	1.771	3613.35	3680.08	3774.02
$10X10^{-3}$	9.32	9.82	9.86	60.1	61.7	61.9	2.017	1.887	1.851	3576.95	3661.52	3706.01

Solvent : Cyclohexane

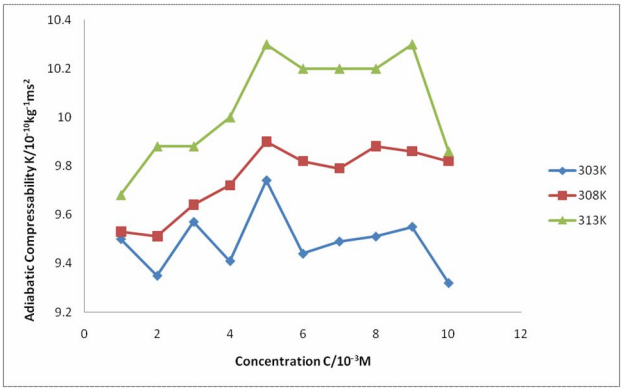

Fig 2. Plot of Adiabatic compressibility Vs Concentration for Mesitylene+ 1-propanol at different Temperature.

Solvent : Cyclohexane

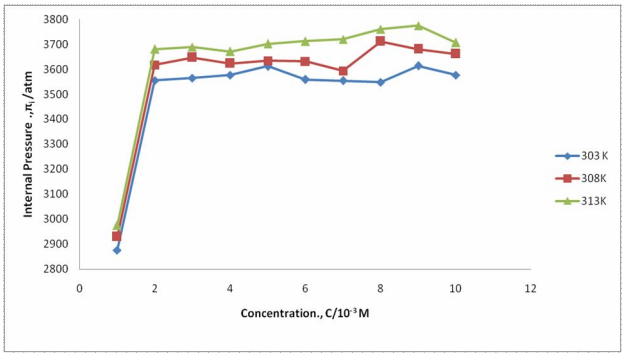

Fig-3: Plot of Internal pressure Vs Concentration for Mesitylene+ 1-propanol at different Temperature.

Solvent : Cyclohexane

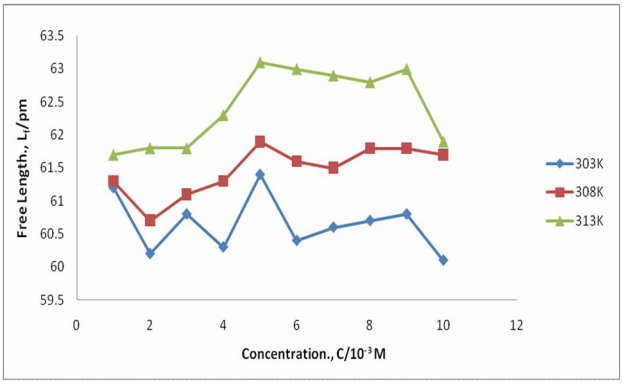

Fig-4: Plot of Free length Vs Concentration for Mesitylene + 1-propnol at different Temperature

Cohesive Energy (CE) values of the system are tabulated in table 3.

Table-3: Values of Absorption Coefficient, Viscous Relaxation Time, Available Volume & Cohesive Energy of the system: Mesitylene + 1-Propanol + Cyclohexane

Concentration	Absorption Coefficient			Viscous Relaxation Time 10^{-3}s.			Available Volume $V_a/10^{-5}$ m^3			Cohesive Energy KJ/mole		
	Temperature (K)			Temperature (K)			Temperature (K)			Temperature (K)		
	303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K
$1X10^{-3}$	1.44	1.49	1.54	8.808	9.041	9.258	3.472	3.500	3.594	70.848	70.373	69.800
$2X10^{-3}$	1.40	1.45	1.55	8.627	8.851	9.244	2.790	2.876	3.046	58.568	58.030	57.713
$3X10^{-3}$	1.43	1.48	1.54	8.713	8.910	9.167	2.896	2.949	3.058	58.692	57.830	57.626
$4X10^{-3}$	1.41	1.48	1.57	8.613	8.932	9.252	2.830	2.977	3.115	58.337	58.145	57.931
$5X10^{-3}$	1.49	1.53	1.64	9.020	9.179	9.604	2.973	3.045	3.216	58.059	57.979	57.613
$6X10^{-3}$	1.40	1.52	1.64	8.607	9.115	9.590	2.839	3.011	3.201	58.378	58.281	57.828
$7X10^{-3}$	1.42	1.51	1.65	8.728	9.118	9.686	2.850	2.980	3.187	58.639	58.287	57.859
$8X10^{-3}$	1.41	1.58	1.66	8.643	9.400	9.733	2.867	3.047	3.181	58.671	58.378	57.665
$9X10^{-3}$	1.46	1.56	1.68	8.878	9.322	9.809	2.894	3.034	3.208	58.299	58.211	57.574
$10X10^{-3}$	1.40	1.54	1.56	8.642	9.269	9.344	2.784	3.014	3.022	58.468	58.379	57.877

Solvent : Cyclohexane

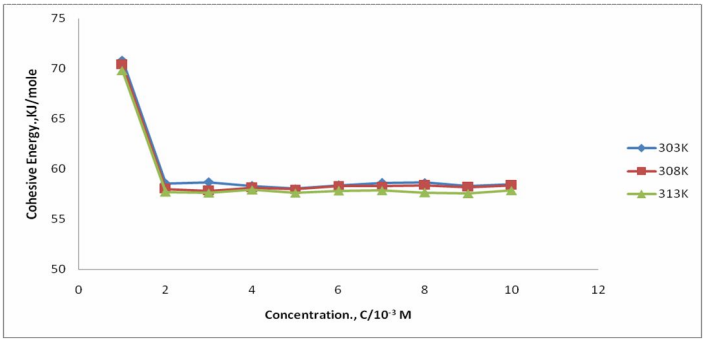

Fig-5: Plot of Cohesive Energy Vs Concentration for Mesitylene + 1-propnol at different Temperature

The Cohesive Energy is a measure of attraction between molecules of the components. The decrease in Cohesive Energy values with increase in concentration and temperature shows a weaker molecular interactions are present in this system.

Molecular Interaction parameter values are computed and tabulated in Table 4.

Table-4: Values of Lenard Jones Potential, Free Energy of Activation, Molecular Interaction parameter & Formation constant of the system: Mesitylene + 1-Propanol + Cyclohexane

Concentration	Lenard Jones Potential			Free Energy of Activation			Molecular Interaction Parameter			Formation constant		
	Temperature (K)			Temperature (K)			Temperature (K)			Temperature (K)		
	303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K
$1X10^{-3}$	11.279	10.922	10.108	4.739	4.811	4.877	-4.399	-5.333	-7.554	99.5	93.9	83.8
$2X10^{-3}$	12.078	11.101	9.633	4.681	4.752	4.872	-2.390	-4.863	-8.910	60.1	47.3	37.5
$3X10^{-3}$	11.072	10.292	9.380	4.709	4.711	4.849	-4.940	-7.042	-9.653	51.3	46.6	42.5
$4X10^{-3}$	11.500	10.211	9.104	4.677	4.777	4.875	-3.835	-7.268	-10.480	43.9	37.4	33.4
$5X10^{-3}$	10.438	9.857	8.505	4.804	4.853	4.978	-6.643	-8.267	-12.330	32.1	30.2	26.7
$6X10^{-3}$	11.527	10.086	8.548	4.675	4.834	4.974	-3.767	-7.619	-12.190	32.5	27.7	24.2
$7X10^{-3}$	11.624	10.622	8.723	4.714	4.835	5.001	-3.524	-6.141	-11.640	28.9	25.8	21.7
$8X10^{-3}$	11.370	9.620	8.587	4.687	4.918	5.015	-4.169	-8.952	-12.070	25.5	21.6	19.9
$9X10^{-3}$	10.990	9.848	8.371	4.761	4.899	5.036	-5.159	-8.294	-12.750	22.3	20.2	18.0
$10X^{-3}$	12.010	10.068	9.809	4.686	4.880	4.902	-2.562	-7.672	-8.407			

Solvent : Cyclohexane

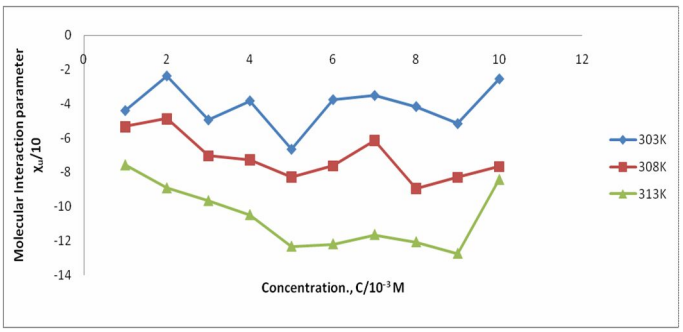

Fig-5: Plot of Molecular interaction Vs Concentration for Mesitylene + 1-propnol at different Temperature

The above table values are positive (or) negative depending on the concentration. Thus, there is a weak interaction between the donor and 1-propanol molecules in Cyclohexane solution. As the number of $–CH_3$ group in Mesitylene implies that dipole – induced dipole interactions is weaker in higher hydrocarbons (Mesitylene) owing to its decrease polarisabilities with the increase of $–CH_3$ group.

The formation values (K) for this system are represented in Table 5.

System	Mean K Value
Mesitylene +1-Propanol at 303K	44.01
Mesitylene + 1-Propanol at 308K	38.96
Mesitylene + 1-Propanol at 313K	34.18

The formation constant decreases with decrease in polarisability of donor molecules. Therefore, increase in polarisability of donor decreases the ease of complexation. But in the present study involved the dipole – Induced dipole interactions is weaker in hydrocarbons (Mesitylene) owing to its decreases polarisabilities with the increase of $–CH_3$ groups.

Conclusion:

The present study involves the weak interaction induced Dipole – Dipole between Mesitylene and 1-Propanol respectively. It also deals with the formation of donor – acceptor complexes between them. The study finally concludes that interaction and stability of the complexes decreases with increase of temperature.

References:

1. Dash AK, and Paikaray R. Acoustical study in binary liquid mixture containing dimethyl acetamide using Ultrasonic and Viscosity probes. Der Chem., 2014, 5(1) : 81-88.
2. Palani R, Saravanan S, Kumar R. Ultrasonic studies on some ternary organic liquid mixtures at 303K, 308K and 313K', RASAYAN. J.Chem., 2009, 2(3): 622-629.
3. Paikaray R, Mohanty N. Evaluation of Therodynamical Acoustic Parameters of Binary mixtures of DBP with Toluene at 308K and at Different Frequencies. Research Journal of Chemical Sciences., 2013, 3(5) : 71-82.
4. Mistry AA, Bhandakkar VD, Chimankar OP. Acoustical studies on ternary mixtures of Toluene in Cyclohexane and nitrobenzene at 308K using ultrasonic technique. J. of Chem. And Pharm. Res., 2012, 4(1) : 170-174.
5. Thirumaran S, Thenmozhi P. Study of Molecular Interaction in ternary liquid mixtures by Ultrasonic Velocity Measurements. Asian Journal of Applied Sciences., 2010.
6. Hemalatha B, Vasantharani P. Ultrasonic studies on ternary liquid systems at different temperatures. Archives of Applied Science and Research., 2013, 5 (3): 31-37.
7. Thirumaran S, Saradha Devi S. Acoustic studies on Primary Alcohols in p-xylene with Nitrobenzene at 303K". Archives of Applied Science Research., 2009, 1 (2) : 128-141.
8. Thiyagarajan R, Palaniappan L. Molecular Interaction study of two aliphatic alcohols with Cyclohexane. Indian Journal of Pure and Applied Physics., 2008, 46 : 852-856.
9. Thirumaran S, Earnest Jayakumar J. Ultrasonic study of n-alkanols in Toluene with nitrobenzene. Indian Journal of Pure and Applied Physics., 2009, 36 : 265-272.
10. Manoj Ku.Praharaj, Abhiram Satapathy. Ultrasonic analysis of intermolecular interaction in the mixture of benzene with N,N-dimethylformamide and Cyclohexane at different temperatures Journal of Chemical and Pharmaceutical Research., 2013, 5(1): 49-56.
11. Sangita Sharma, Khushbu Thakkar. Volumetric and Viscometric and Excess properties of Binary Mixtures of 1-Iodobutan with Benzene, Toluene, o-Xylene, m-Xylene, p-Xylene and Mesitylene at temperatures from 303.15K to 313.15K.
12. Nain AK, Chandra P, Pandey JD, Gopal S. Densities, Refractive indices and excess properties of binary mixtures of 1,4-dioxane with benzene, toluene, o-Xylene, m-Xylene, p-Xylene and Mesitylene at temperatures from (288.15 to 318.15K). Journal of Chemical and Engineering Data., 2008, 53(11) : 2654-2665..
13. Rita Mehra, Meenakshi Pancholi, Avneesh K, Gaur. Ultrasonic and Thermodynamic studies in ternary liquid system of Toluene + 1-dodecanol + Cyclohexane at 298, 308 and 318K.
14. Kannappan V, Jayasanthi. J. Acous. Soc., Ind., 2001, (29):192.
15. Chidambaravinayagam S, Ph.D., Thesis. University of Madras. India, 2007.

*****