International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064, Impact Factor (2013): 4.438
www.ijsr.net

Visco Metric, Volumetric and Acoustic Studies in Ternary Mixture of Dimethyl Acetamide and Diethyl Ether in an Aprotic Solvent

Ashok Kumar Dash[1], Rita Paikaray[2]

[1]Department of Physics,L.N College.Patkura.Kendrapara.Odisha,India

[2]Department of Physics, Ravenshaw University Cuttack, Odisha,India

Abstract: ***The ultrasonic velocity (U), density (ρ) and coefficient of viscosity (η) of the ternary mixture of dimethyl acetamide and diethyl ether in an aprotic solvent acetone at frequencies 2MH$_Z$, 4MHz, 6MH$_Z$ and 8MH$_Z$ have been measured at temperature 308K. Adiabatic compressibility (K_s), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i) and their respective excess values have been computed for entire range of mole fraction and are interpreted to explain molecular interaction occurring in the liquid mixture. Relaxation time (τ), excess enthalpy (H^E) and absorption coefficient (α/f^2) have been calculated and discussed. The negative values of excess adiabatic compressibility (K_s^E) and excess free length (L_f^E) indicate the existence of strong molecular interactions due to charge transfer, dipole-dipole, dipole-induced dipole interactions and formation of hydrogen bonds.***

Keywords: Ternary mixture, ultrasonic velocity, free volume, internal pressure, relaxation time, excess enthalpy, and absorption coefficient

1. Introduction

The acoustical study of liquid plays an important role in understanding the nature and strength of molecular interaction. A large number of studies have been made on the molecular interaction in liquid mixture by various methods like Ultraviolet, Dielectric constant, Infrared, Raman Effect, Nuclear magnetic resonance and Ultrasonic method. Recently, ultrasonic method has become a powerful tool to provide information regarding the physical and chemical properties of liquid system. The ultrasonic study in organic liquid mixture is interesting to discuss non-linear behavior with respect to concentration and frequency. The present investigation is related on study of molecular interaction internary liquid mixture of dimethyl acetamide (DMAC) which is a dipolar aprotic solvent with high boiling point and good thermal and chemical stability. Ultrasonic studies may throw more light on the molecular interaction to understand the behavior of liquid molecules in ternary mixture of dimethyl acetamide, diethyl ether and acetone. The study of DMAC is important because of its utilization in industry and medicine. It is highly soluble in a variety of polar and non-polar liquids and readily suitable to explore solvent-solvent interactions. Acetone is also an important dipolar aprotic solvent used in industry and pharmaceuticals. Diethyl ether is a non-polar liquid used as a solvent in the production of cellulose plastics. The non-linear deviation in the velocity versus mole fraction in liquid mixture of DMAC is taken as an indication of the existence of interactions between different liquid molecules. The physiochemical properties of liquid mixture can be studied by the non-linear variation of ultrasonic parameters with concentration in the liquid mixture [1-8].

2. Experimental Procedure

The ternary liquid mixtures of various concentrations in mole fraction were prepared by taking chemicals of analytical grade (E Merck) which were used as such without further purification. The mole fraction of acetone was kept fixed arbitrarily at X_2=0.4. The mole fraction of DMAC was increased from 0 to 0.6 while the mole fraction of diethyl ether was decreased from 0.6 to 0 so as to have the mixture of different compositions. Liquid mixtures of different mole fractions were prepared with a precision of 0.0001g using an electronic digital balance. Density (ρ) of liquid mixture was determined by a specific gravity bottle of 10ml capacity. Coefficient of viscosity (η) of pure liquids and liquid mixture was determined by an Ostwald's viscometer.The ultrasonic velocity **(U)** was measured by a multifrequency interferometer(Mittal - type) with a high degree of accuracy operating at different frequencies. An electronically operated constant temperature water bath is used to circulate water through the double walled measuring cell made up of steel containing the experimental liquid mixture at temperature 308K.

3. Theory

Using the measured data the acoustical parameters such as adiabatic compressibility (K_s) intermolecular free length (L_f), free volume (V_f) and internal pressure (π_i) have been calculated from the following relations.

$$K_s = (U^2\rho)^{-1} \tag{1}$$
$$L_f = k\,(K_S)^{1/2} \tag{2}$$
$$V_f = (MU/K\eta)^{3/2} \tag{3}$$
$$\pi_i = bRT(K\eta/U)^{1/2}(\rho^{2/3}/M^{7/6}) \tag{4}$$

Where k is a temperature dependent constant, M is the effective molecular weight, K is a temperature independent constant which is equal to 4.28 × 10^9 for all liquids. R is universal gas constant, b is the cubic packing factor which is equal to 2 for all liquid mixtures.

The excess values of the above acoustical parameters have been calculated from the following relations.

$$A^E = A_{exp} - (X_1A_1 + X_2A_2+X_3A_3) \quad (5)$$

Where X_1, X_2 and X_3 are mole fractions of DMAC, acetone and diethyl ether respectively and A is any acoustical parameter.

Relaxation time(τ),excess enthalpy(H^E) and absorption coefficient(α/f^2), have been calculated from the following relations.

$$\tau = (4/3)\, K_s\eta \quad (6)$$

$$H^E =(X_1\, \pi_{i1}\, Vm_1 + X_2\, \pi_{i2} V_{m2} +X_3\, \pi_{i3}\, V_{m3}) - \pi_i V_m \quad (7)$$

$$\alpha/f^2 = 2\pi^2\tau/U \quad (8)$$

4. Results and Discussion

The experimental values of density ρ, coefficient of viscosity η and ultrasonic velocity U at 308K for frequencies 2MHz, 4MHz, 6MHz and 8MHz for pure liquids and ternary liquid mixture were used to calculate the acoustical parameters and the relevant data are displayed graphically in Figures- 1 to 16.

The increase in density ρ with the increase in mole fraction of DMAC as shown in Figure-1 indicates the presence of solvent-solvent interactions [9]. The increase in coefficient of viscosity η with the increase in mole fraction of DMAC as shown in Figure-2 indicates the presence of solute-solvent interactions. The increase in ultrasonic velocity U with the increase in mole fraction of DMAC as shown in Figure-3 at a particular frequency may be due to the structural changes occurring in the ternary mixture resulting in the increase in intermolecular interactions. The variations of adiabatic compressibility Ks, intermolecular free length L_f , free volume V_f and internal pressure π_i with the increase in mole fraction of DMAC are shown graphically in Figures-4 to 7. The decrease in adiabatic compressibility, intermolecular free length and free volume while increase in internal pressure with the increase in concentration of DMAC reveals the presence of specific interactions between the components in the binary liquid mixture.

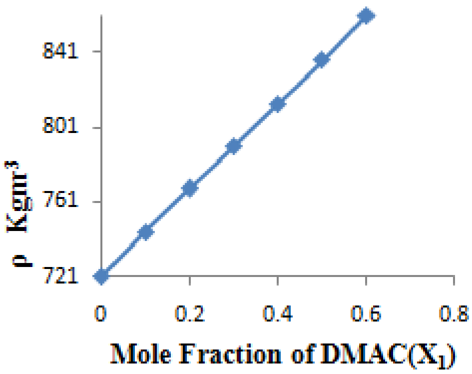

Figure 1: Variation of ρ Versus X_1

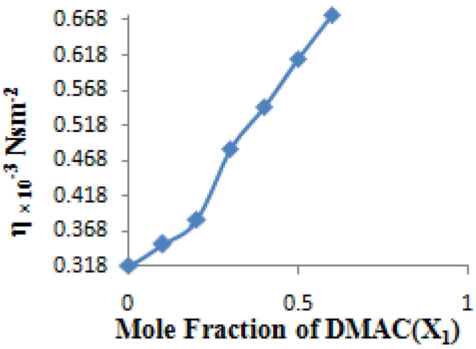

Figure 2: Variation of η Versus X_1

The ultrasonic velocity decreases by increasing the frequency from 2MHz, to 8MHz at a fixed concentration of DMAC. The decrease in ultrasonic velocity may be due to the decrease in molecular interaction in the ternary liquid mixture. Consequently the values of adiabatic compressibility, intermolecular free length and internal pressure increase and free volume decreases with the increase in frequency for a particular mole fraction of DMAC.

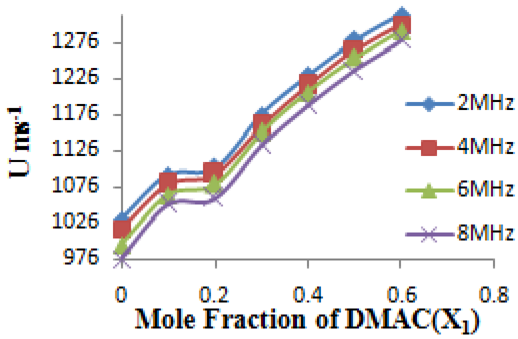

Figure 3: Variation of U Versus X_1

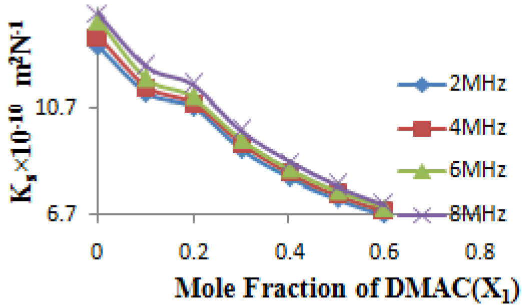

Figure 4: Variation of K_s Versus X_1

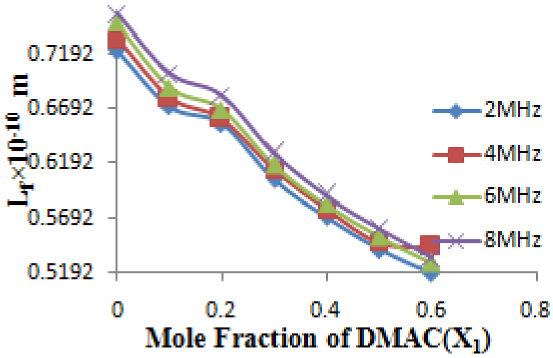

Figure 5: Variation of L_f Versus X_1

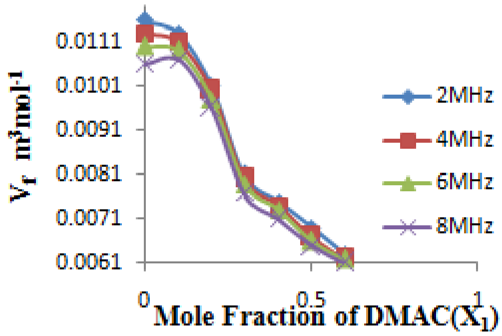

Figure 6: Variation of V_f Versus X_1

The values of free volume V_f decreases with the increase in mole fraction of DMAC for a particular frequency as shown in Figure-6. The decrease in free volume with the increase in concentration of DMAC is because of (i) contraction due to the free volume difference of unlike molecules. (ii) contraction due to the hydrogen bond formation between unlike molecules. (iii) specific interactions between unlike molecules in the liquid mixture.

Figure-7 show that internal pressure π_i increases with the increase in mole fraction of DMAC for a particular frequency. The increase in internal pressure with the increase in concentration of DMAC indicates the increase of cohesive forces in the ternary mixture.

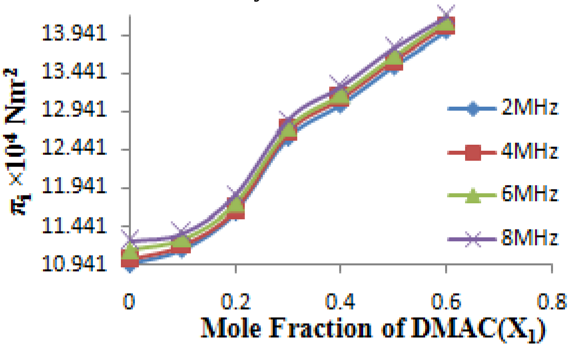

Figure 7: Variation of π_i Versus X_1

The excess values of coefficient of viscosity η^E are negative for the mole fraction of DMAC between 0.1 to 0.6 and positive in the absence of DMAC as shown in Figure-8 for all frequencies. The negative excess values of η^E indicate the presence dispersion, induction and dipolar forces in ternary liquid mixture [10].

Figure-9 show that the values of excess velocity U^E are positive for lower mole fractions of DMAC and negative for higher mole fractions of DMAC for all frequencies which indicate the presence strong interactions at lower concentration and dispersion interaction at higher concentration of DMAC in the ternary mixture.

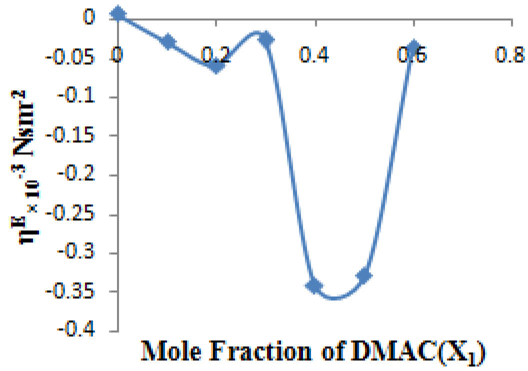

Figure 8: Variation of η^E Versus X_1

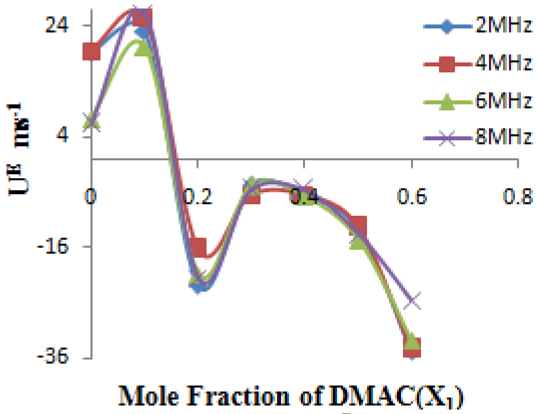

Figure 9: Variation of U^E Versus X_1

The values of K_s^E are negative for the entire range of mole fraction of DMAC for all frequencies as shown in Figure-10. The negative value of K_s^E predict the existence of strong molecular interactions in the ternary liquid mixture due to the formation of hydrogen bonds.

It is seen from Figure-11 that the values of excess free length are negative for whole range of the mole fraction of DMAC for all frequencies. The negative excess values of L_f^E indicate the existence of strong molecular interactions due to charge transfer, dipole-induced dipole, dipole-dipole interactions and formation of hydrogen bonds.

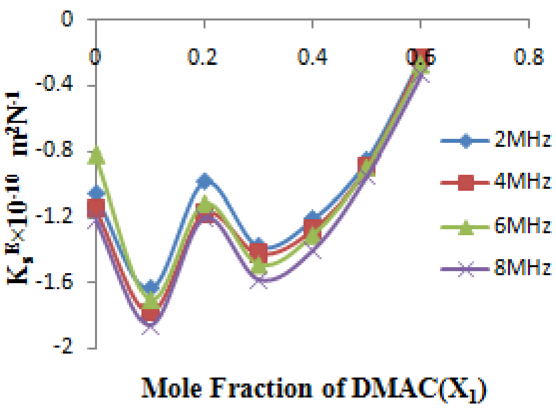

Figure 10: Variation of K_s^E Versus X_1

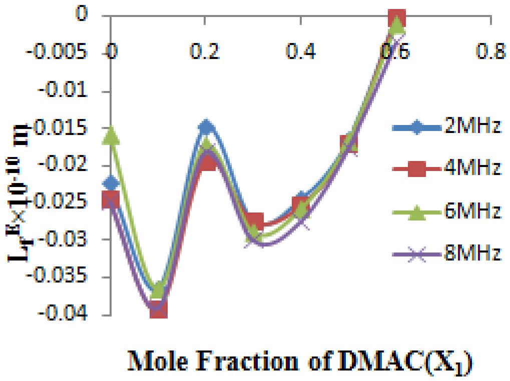

Figure 11: Variation of L_f^E Versus X_1

Figure-12 show that the values of excess free volume V_f^E are positive or slightly negative for lower concentration of DMAC which indicate the presence of weak interactions due to the dispersive forces, steric hindrance of component molecules, unfavorable geometric fitting and electrostatic repulsion. The values V_f^E are negative for higher concentration of DMAC which indicate the presence of strong interactions in the ternary liquid mixture due to the specific interactions between the component molecules and physical forces like dipole-dipole or dipole-induced dipole interactions or Vanderwaal's forces[11].

The values of excess internal pressure π_i^E are negative for lower concentration of DMAC and positive for higher concentration of DMAC as shown in Figure-13 in the ternary mixture which indicate the presence of dispersion interactions at lower concentration and strong interactions at higher concentration of DMAC in the liquid mixture [12].

It is found that the values of excess velocity, excess adiabatic compressibility, excess free length and excess free volume are changed with the increase in frequency due to the decrease in ultrasonic velocity in the ternary liquid mixture.

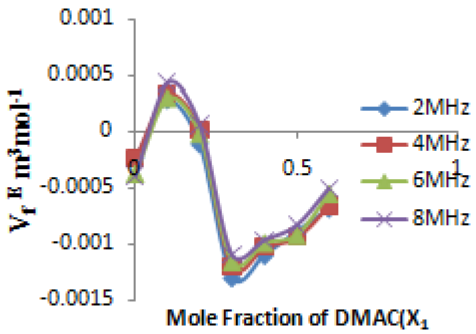

Figure 12: Variation of V_f^E Versus X_1

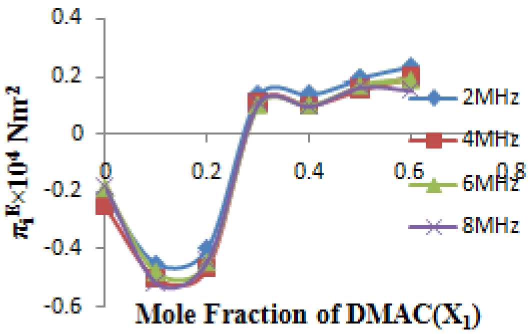

Figure 13: Variation of π_i^E Versus X_1

It is observed from Figure-14, that the relaxation time τ varies non-linearly with the increase of mole fraction of DMAC for a fixed frequency. The relaxation time τ increases with the increase in frequency for a fixed mole fraction DMAC which indicate the decrease in molecular interaction with rise in frequency. The relaxation time is in the order of 10^{-12}s may be due to the structural relaxation process showing the presence of molecular interactions and in such a case it is suggested that the molecules get rearranged due to co-operative process.

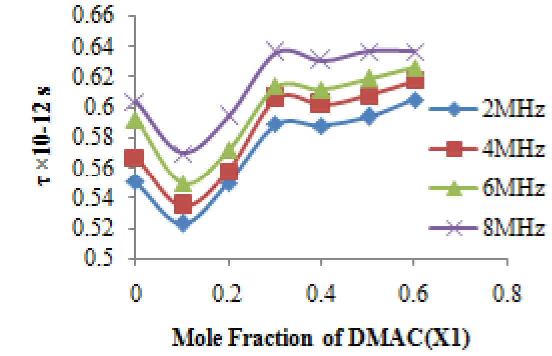

Figure 14: Variation of τ Versus X_1

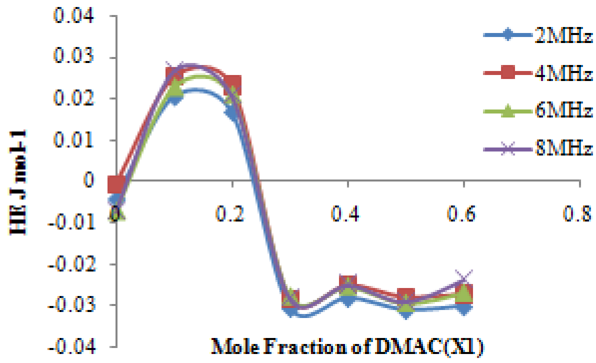

Figure 15: Variation of H^E Versus X_1

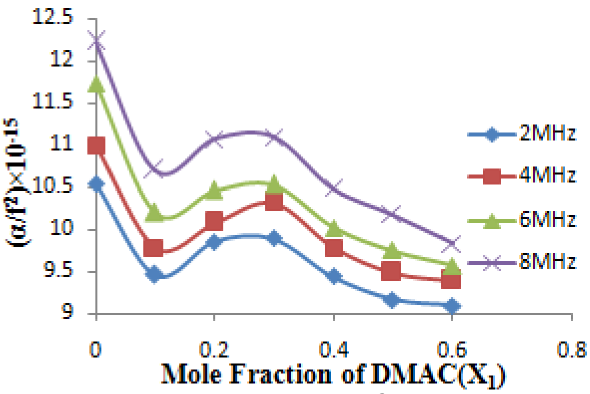

Figure 16: Variation of α/f^2 Versus X_1

Figure-15 show that the values of excess enthalpy H^E are positive or slightly negative for lower mole fraction of DMAC and negative for higher mole fraction of DMAC for all frequencies which indicate the presence of dispersion interactions at lower concentration and strong interactions at higher concentration of DMAC in the ternary mixture [13].
The values of absorption coefficient α/f^2 vary non-linearly with the increase of mole fraction of DMAC as shown in Figure-16 for a fixed frequency which indicate the presence of molecular interaction [14]. The increase in absorption

coefficient with the increase in frequency for a fixed concentration of DMAC indicates the reduction in molecular interaction in the ternary liquid mixture.

5. Conclusion

It is concluded that there exists hydrogen bonding, charge transfer, dipole-dipole and dipole-induced dipole interactions and Vander Waal's forces in the ternary liquid mixture of DMAC and diethyl ether in an aprotic solvent acetone. Dispersive forces, steric hindrance of component molecules, unfavorable geometric fitting and electrostatic repulsion are also found to exist in the liquid mixture. Further, it is concluded that the molecular interaction increases with the increase in concentration of DMAC for a fixed frequency and decreases with the increase in frequency for a fixed concentration of DMAC in the ternary mixture.

6. Acknowledgement

The author Ashok Kumar Dash is thankful to the University Grants Commission (ERO), Kolkata, India for providing financial support in the form of Minor Research Project grant.

References

[1] A K Dash and R Paikaray**, Study of molecular interaction in binary liquid mixture of dimethyl acetamide and acetone using ultrasonic probe** *Advances in Applied Science Research*, **4(3) (**130-139) (2013)

[2] A K Dash and R Paikaray, **Acoustical study on ternary mixture of dimethyl acetamide (DMAC) in diethyl ether and isobutyl methyl ketone at different frequencies,** *Physics and Chemistry of Liquid*, **, 51(6)**, 749-763 (2013)

[3] A K Dash and R Paikaray, **Ultrasonic Study on Ternary Mixture of Dimethyl Acetamide (DMAC) in Diethyl ether and Acetone**,*Research Journal of Physical Sciences*,**1(3),(**12-20) (2013)

[4] J N Ramteke, **Ultrsonic Study on Molecular Interaction in Binary liquid Mixture containing α-picolin in ethanol at 301.15K**, *Pelagia Research Library*,**3(3)**,(1832-1835) (2012)

[5] A. Ali and A. K. Nain, **Ultrsonic Study of Molecular Interaction in Binary liquid Mixtures at 30^{0}C**, *PRAMANA*, **58(4) (**696-701) (2002)

[6] V Kanappan&J Santhi , **Ultrasonic study of induced dipole-dipole interactions in binary liquid mixtures** , *Indian Journal of Pure & Applied Physics*,**(43)** (750-754) (2005)

[7] K Rajagopal and S Chenthilnath, **Excess thermodynamic studies of binary mixtures of 2-methyl 2-propanol with ketones**, *Indian Journal of Pure & Applied Physics*,**(48)** (326-333) (2010)

[8] A K Gupta, K Kumar and B K Karn, **Ultrasonic studies of binary liquid mixtures of o-cresol with ethylmethyl ketone, acetone acetophenone and ethylacetate**, *J. Ind. Council Chem*. **26** (77-81) (2009)

[9] R Natrajan, and P Ramesh, **Ultrasonic velocity determination in binary liquid mixtures**, *J. Pure appl. And Ind. Phys*, **1(4**), (252- 258) (2011)

[10] R. Palani, S. Saravanan and R. Kumar, **Ultrasonic studies on some ternary organic liquid mixtures at 303, 308 and 313K**, *RASAYAN J. Chem.***2(3),** 622-629 (2009)

[11] S Thirumaran and M Rajeswari, **Acoustical studies on binary liquid mixtures of some aromatic hydrocarbons with dimethylsulphooxide (DMSO) at 303.15K**, *Scholars Research Library* **2(2)** (149-156) (2011)

[12] S R Mirgane and S S Patil,**An ultrasonic study of acrylates with dodecane-1-ol at 313.15K**, *Der Chemica Sinica***, 3(6)** (1490-1499) (2012)

[13] R Mehra, M Pancholi and A K Gaur, **Ultrasonic and thermodynamic studies in ternary liquid system of toluene+1-dodecanol+cyclohexane at 298,308 and 318K**, *Archives of Applied Science Research***, 5 (1) (**124-133) (2013)

[14] R Mehera and B B Malav,**Acoustic,volumetric and visco metric studies in aqueous galactose solution in the presence of sodium chloride 298,308 and 318K**, *Research of Journal Pharmaceutical Biological and Chemical Sciences*, **2(3)** (709-719) (2011)