Study of Thermodynamical Acoustic Parameters of Binary Mixture of DBP with *O*-Xylene at 308k and at Different Frequencies

N.Mohanty[1], R.Paikaray[2]

[1, 2]P.G .Department of Physics, Ravenshaw University, Cuttack-753003, Odisha, India

Abstract: ***Ultrasonic investigation of molecular interactions in a binary mixture of Di-n-butyl phthalate (DBP) with o-xylene is carried out at different frequencies (1MHz, 3MHz, 5MHz &7MHz) at temperature 308K. The experimental measured values of density (ρ) and ultrasonic velocity (U) of the binary mixture has been used to compute the different acoustic parameters like isentropic compressibility (β) intermolecular free length (L_f), acoustic impedance (Z), molar volume (Vm)and their excess values. These acoustic parameters and their excess values are used to access and explain the nature and strength of molecular interaction of DBP and toluene.Relative association (RA), interaction parameter (χ) are also computed for the binary mixture to study the strength and merits of the molecular interactions present between the unlike molecules of the binary mixture.***

Keywords: Binary mixture, ultrasonic velocity, isentropic compressibility, intermolecular free length and acoustic impedance.

1. Introduction

Ultrasonic study of velocity, density along with acoustic parameters relating these variables with their respective excess values in liquid and liquid mixture are essential to understand the molecular interactions between the unlike molecules to develop theoretical models and applications in industrial processes. Propagation of ultrasonic waves in any substance reveals many physico-chemical properties of the substance. Mixed solvents rather than pure solvents have a wide range of applications in various industries and technology [1,2] .

Ultrasonic investigation of liquid mixture consisting of DBP (Polar) and *o*-xylene (non polar) is of considerable importance because of its extensive use in engineering and various industries. Di-n-butyl phthalate ($C_{16}H_{22}O_4$) (DBP) is an odourless, colourless and viscous liquid which does not occur in nature. It has wide spread use throughout the society. The largest use of DBP is as a plasticizer. It is added to hard plastics to make them soft. It is used in printing ink, adhesives, paper coating, film coating, lubricating glass fibre, nail polish, hair spray, perfume solvent, finative, antifoamer, mosquito repellant etc. and above all it is used as a rocket fuel.

A study is carried out in the binary mixture of DBP and *o*-xylene at different frequencies (1MHz, 3MHz, 5MHz and 7MHz), ultrasonic velocity is measured and related parameters are calculated at 308K. These parameters provide qualitative information regarding the nature and strength of interaction in liquid mixtures which has various applications in our society.

2. Theory

The ultrasonic velocity and density of the binary mixture is measured and is used to compute intermolecular free length (L_f), isentropic compressibility (β), acoustic impedance (Z) and their excess values[3] basing on the following relations.

Isentropic compressibility $\beta = 1/\rho c^2$. (1)

Intermolecular free length $L_f = K \rho^{1/2}$ (2)

Acoustic impendence, $Z = \rho C$ (3)

Molar Volume , $V_m = (X_1M_1 + X_2M_2)/\rho$ (4)

$R_A = (\rho / \rho_0)(U_0/U)$ (5)

$\chi = (U/U_{ideal})^2 - 1$ (6)

The excess values have been calculated from the following relation

$A^E = A_{exp} - (X_1A_1 + X_2A_2)$ (7)

Where $X_1$and X_2 are mole fraction of DBP and *o*-xylene respectively.

3. Experimental Details

Binary mixtures of DBP and *o*-xylene were prepared with varying fractions of DBP. Ultrasonic velocity was measured by a single crystal variable path interferometer at different frequencies of 1MHz, 3MHz, 5MHz and 7MHz at 308K. Density was determined with a Pyknometer before preparation of binary mixture.

4. Result and Discussion

The variation of velocity and its excess values of DBP and *o*-xylene at 308K and frequencies 1MHz, 3MHz, 5MHz, and 7MHz are shown in figures -1and 2 respectively. It is observed that ultrasonic velocity increases gradually with increase in mole fraction of DBP up to 0.365 mole fraction of DBP, then decreases and has a maximum depression at equimolar region of DBP+ *o*-xylene. There is a rise in velocity after 0.61 mole fraction of DBP. The variation of velocity with mole fraction of DBP is nonlinear which indicates the existence of molecular association. Nonuniformity in variation indicates the presence of different types of interactions in the mixture. DBP is a polar liquid and *o*- xylene is partial polar. Variation in the velocity may be due to self-association of the solvent molecules and dipole-induced dipole interaction between the component molecules, which is concentration dependent[4]. At equimolar region of the mixture there is a drop in velocity indicating dipole-induced dipole force dominated by dispersive force and the molecular association breaks which makes an increase in free length and decrease in velocity. With increase in DBP concentration, dipole-induced dipole interaction increases making the system less compressible resulting increase in velocity. The dipole-induced dipole is confirmed by the nonlinear variation of ultrasonic velocity as in other liquid mixture of polar and non polar liquids[5]. Increase in frequencies weakens the interaction which may be due to increase in agitation between molecules resulting decrease in ultrasonic velocity at higher frequencies.

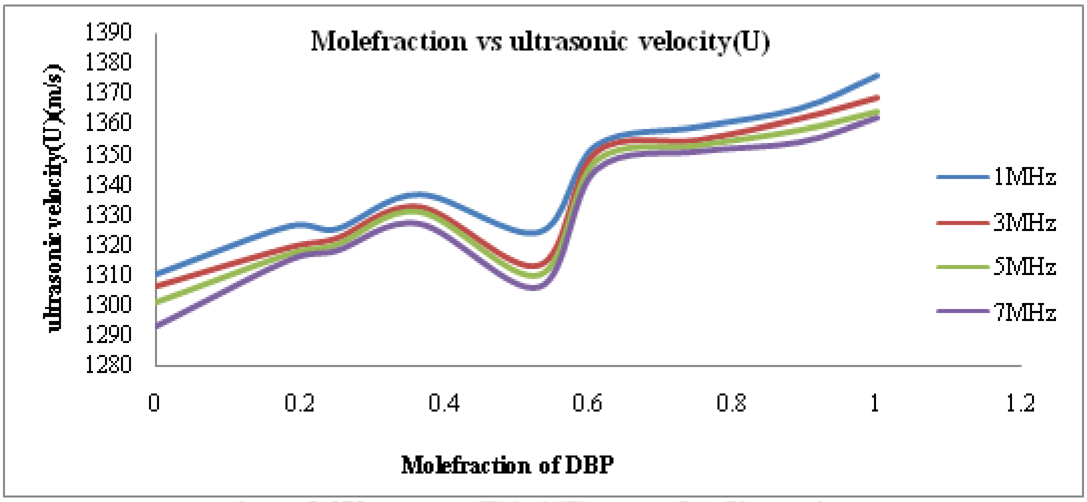

Figure 1: Variation of Ultrasonic velocity (U) vs. Mole fraction of DBP

Variation of excess velocity (U^E) in all four frequencies shows both positive and negative deviation indicating irregular behavior of liquid mixture. Around 0.5 mole fraction, the deviation is negative and maximum suggesting the presence of weak interactions. It is observed that excess velocity (U^E) increases at higher frequencies indicating weak interactions at higher frequencies.

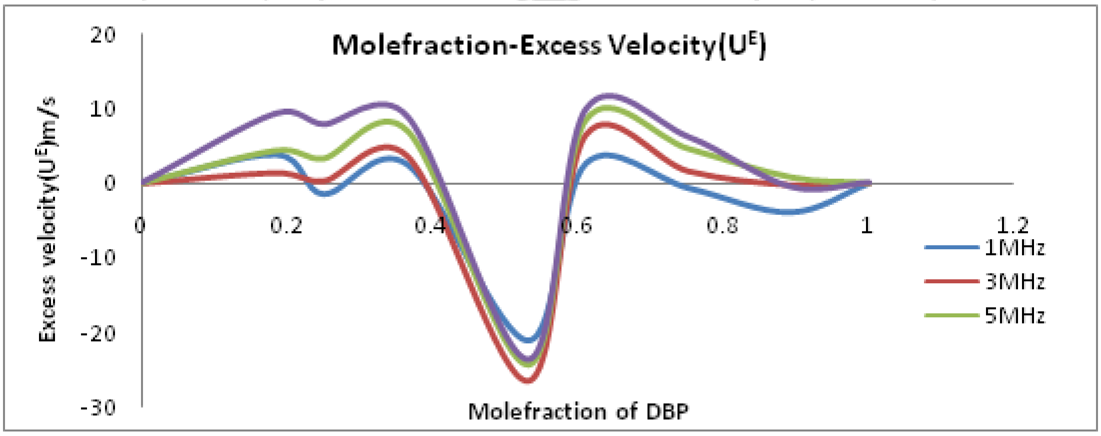

Figure 2: Variation of Excess Ultrasonic velocity vs. Mole fraction of DBP

Variation of acoustic impedance with mole fraction DBP is shown in figure-3. It is observed that values of impedance increase with increase in mole fraction DBP non uniformly as in velocity which is in agreement with the theoretical requirement. Increase in impedance with solute concentration can be attributed to the effective solute-solvent interactions. Excess impedance (Z^E) is found to be both positive and negative which is presented in figure-4. The actual value of Z^E depends on the relative strength of two opposing effects of dispersive forces and dipole-induced dipole forces between DBP and *o*-xylene. However, the excess impedance decreases negatively and approaches a sharp minimum around equimolar region of DBP (0.53) and again increases with increases in DBP. The variation trend is almost similar for all frequencies[6].

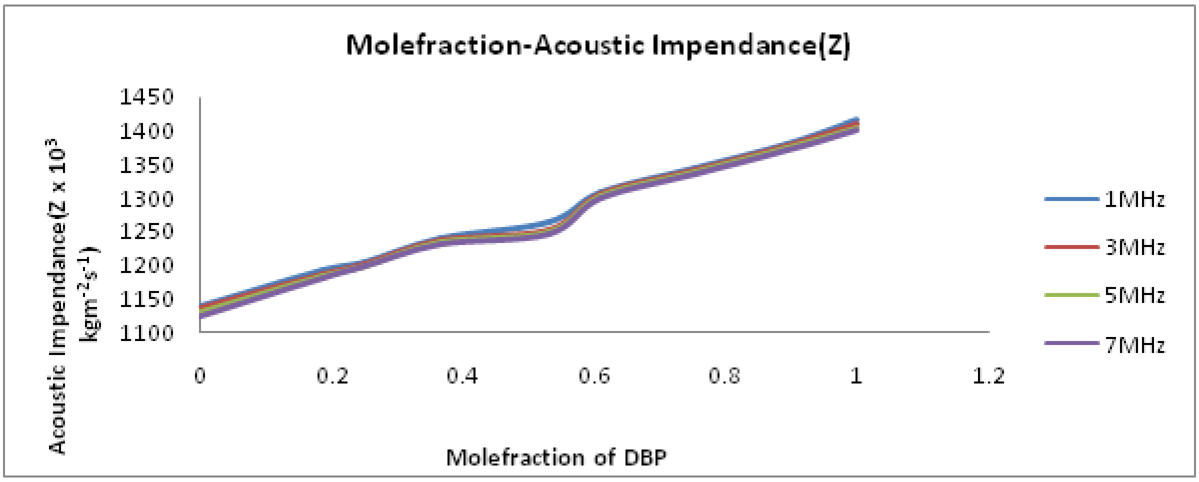

Figure 3: Variation of Mole fraction of DBP vs Acoustic Impedance(Z)

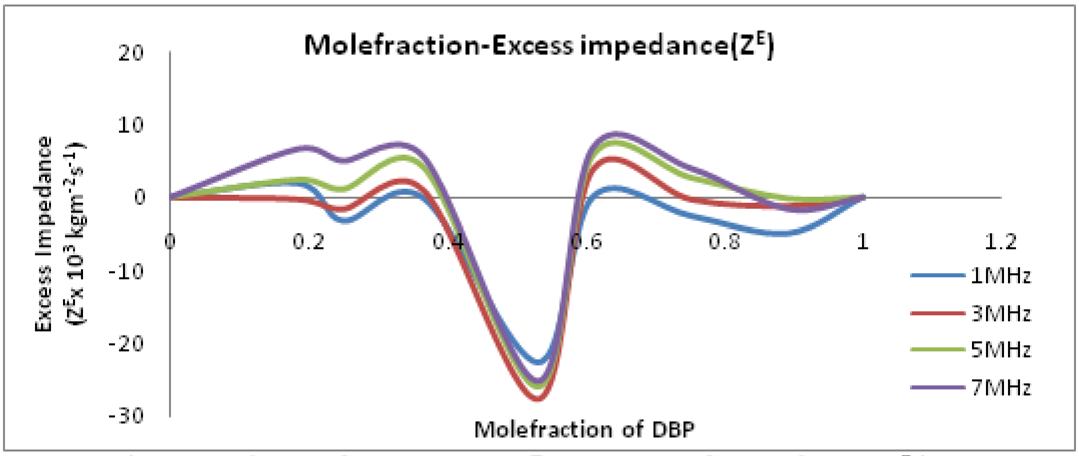

Figure 4: Variation of Mole fraction of DBP vs. excess impedance (Z^E)

Variation of compressibility with mole fraction of DBP and its excess values are shown graphically in figures-5 and 6 respectively. As expected compressibility decreases with increase in concentration of DBP which shows a reverse trend to velocity graph. This behavior of liquid mixture may be due to breaking up of associated clusters of DBP releasing several dipoles, which in turn induces dipole moment in *o*-xylene resulting dipole- induced dipole interaction. The *o*-xylene acts as a structure breaker of DBP. The breaking of associated structure of DBP leads to expansion of volume resulting positive excess compressibility which is observed in equimolar region (0.53 mole fraction of DBP) for all frequencies and slight positive at0.82 mole fraction for 1MHz frequency. The negative values of excess compressibility indicates the structure-forming tendency of hetero-molecular interaction of component molecules of the mixture and may also due to the dominance of dispersive interaction forces [7]. When frequency increases from1MHz to 3MHz to 5MHz to 7 MHz the compressibility in the liquid mixture increases and excess compressibility shows an irregular trend as shown in figure-6.

From figure-7 it is observed that the value of intermolecular free length decreases steadily with increase of mole fraction of DBP and increases with increase in frequency. This indicates the significant dipole–induced dipole interaction between solute and solvent due to which structural arrangement is affected. DBP have higher molar volume, therefore, molar volume of DBP part rises with increase in concentration of DBP and occupies larger spatial arrangement in the molecular core of binary mixture which leaves less intermolecular space in between the associated structure present in the system [3]. The variation of excess free length ($L_f^{\,E}$) given in figure-8 shows similar trend to that of excess compressibility over entire range of composition for all four frequencies.

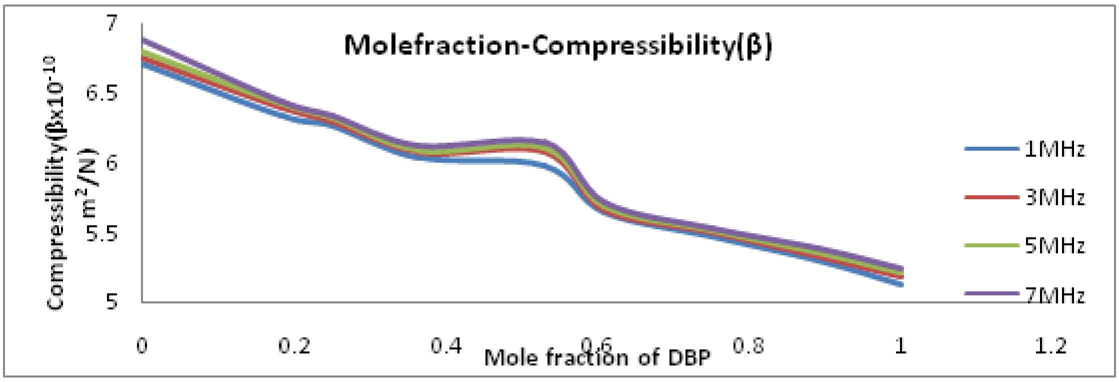

Figure 5: Variation of Mole fraction of DBP vs. compressibility (β).

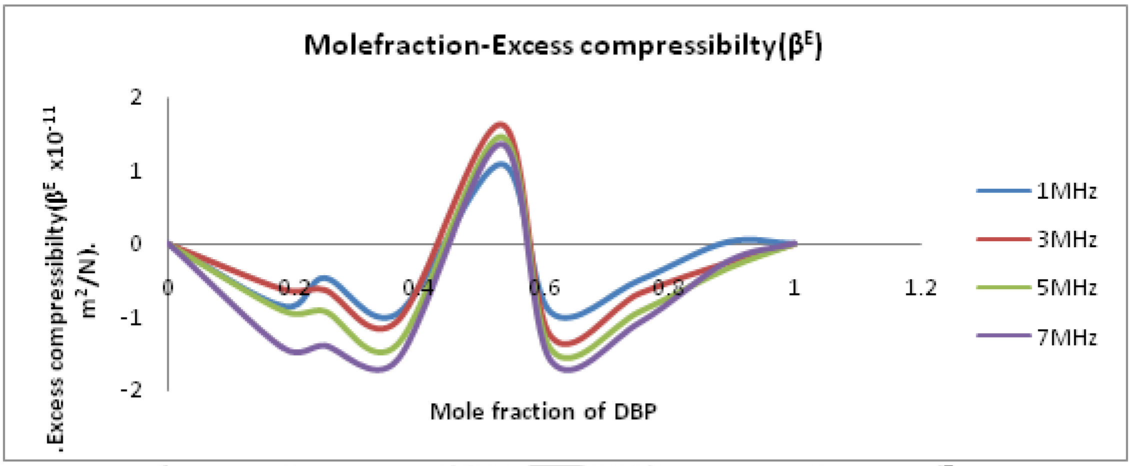

Figure 6: Variation of Mole fraction of DBP vs excess compressibility(β^E)

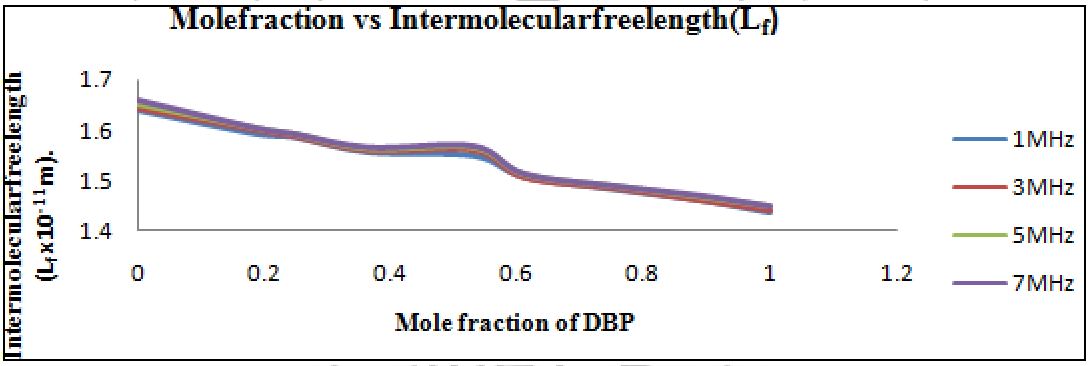

Figure 7: Variation of Intermolecular free length (L_f) vs. Mole fraction of DBP

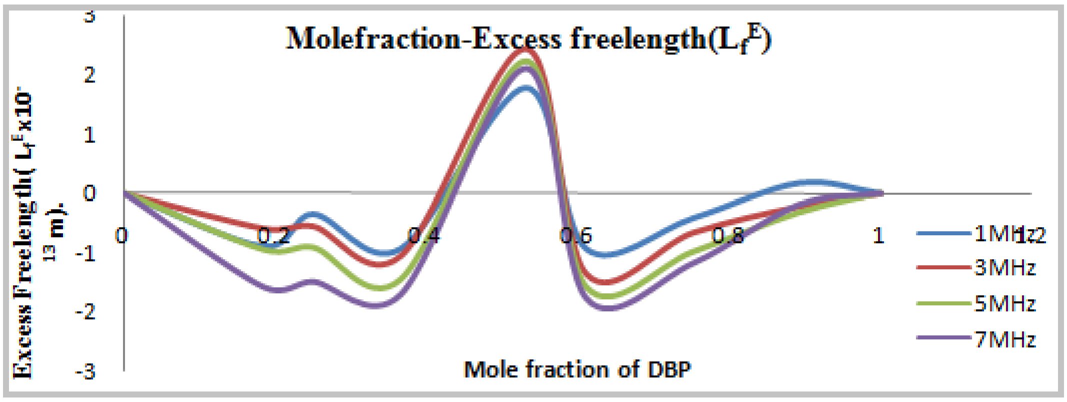

Figure 8: Variation of excess Intermolecular free length (L_f) vs. Mole fraction of DBP

Excess free length shows both negative and positive variations indicating the presence of specific intermolecular interaction in the system. Negative magnitude suggests that the interaction between the component molecules is comparatively strong. Moreover around equimolar region excess free length is positive indicating very weak interaction which results large L_f and less ultrasonic velocity around this region and a weak dipole-induced dipole interaction dominates over breaking up of structural association of DBP. Further, in higher frequency range intermolecular gap decreases which leads to decrease in velocity.

The excess molar volume at four different frequencies for entire range of mole fraction are presented in Figure-9. Excess volume shows a positive deviation over entire range of composition. The strength of interaction is well reflected in the deviations of volume. Excess volume shows the maximum deviation at equimolar region of DBP + *o*-xylene. This expansion of volume may be due to mutual loss of dipolar association of DBP and breaking up of molecular clusters. Positive excess volume indicates existence of weak molecular interactions in the liquid mixture[7, 8].

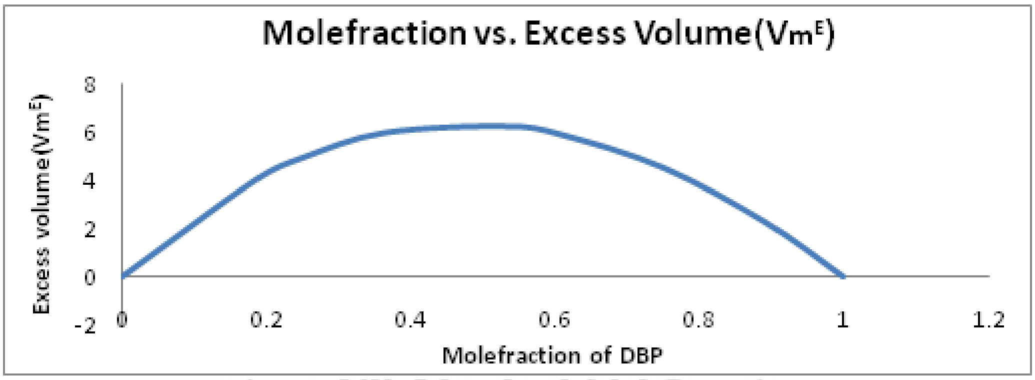

Figure 9: Variation of Excess Molar Volume vs Mole fraction of DBP

Relative association (R_A) are shown in figure-10 for all four frequencies at 308K. R_A increases with the increase in DBP content in the mixture. On the other hand by adding *o*-xylene with DBP, disrupts the dipolar interaction and a very weak dipole-induced dipole interaction exists between the component molecules which are concentration dependent. It is observed from the figure that in all four frequencies the variation of relative association shows irregular trend.

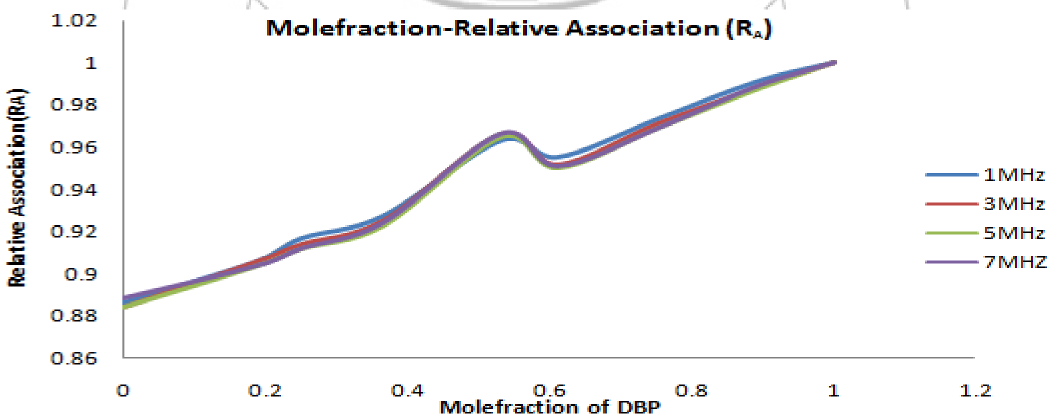

Figure 10: Variation of Relative (R_A) association vs. Mole fraction of DBP.

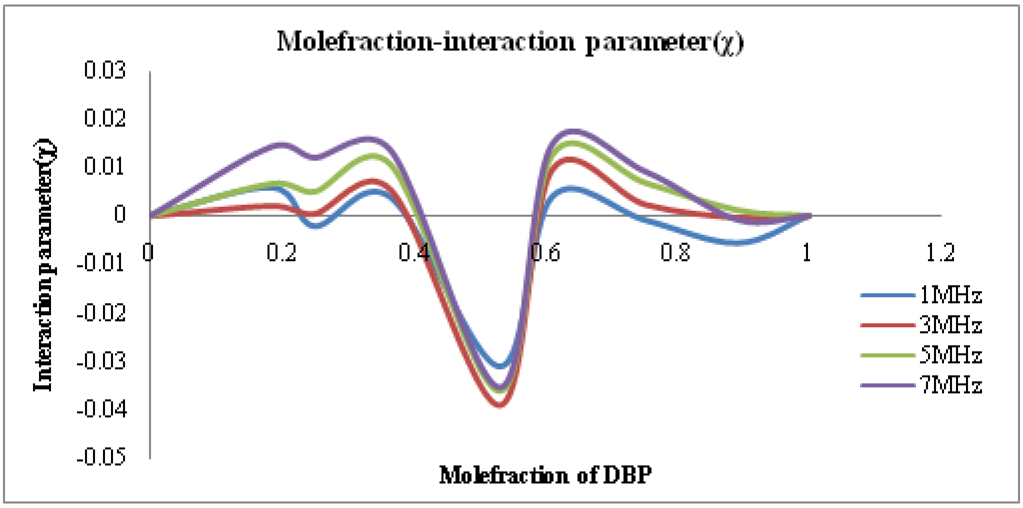

Figure 11: Variation of Interaction Parameter (χ) vs. Mole fraction of DBP.

The variation of interaction parameter shows both positive and negative values for all frequencies(figure-11). It supports the dipole-induced dipole interaction of component molecules which depends on polarizability of interacting molecules[9,10]. Variation of interaction parameter with mole fraction of DBP shows similar trend for all frequencies as in other parameters confirming the existence of specific type of interaction[11].

5. Conclusion

Ultrasonic method is a powerful probe for characterizing the physico-chemical properties and existence of molecular interactions in the liquid mixture. In the binary mixture of DBP + *o*-xylene, the evaluated values of ultrasonic velocity and other derived parameters indicate the presence of molecular interaction between component molecules at constant temperature and at different frequencies. The excess values reveal that there exists a molecular interaction mainly due to dipole-induced dipole interaction. In the present study, the above nonpolar molecules act as structure breaker for associated DBP and there is no complex formation in the liquid mixture. Irregular variations of parameters in DBP +*o*-xylene indicate the presence of specific interactions and this binary mixture is nonideal. Deviation of the excess functions, linear dependence reveals that the extent of interaction decreases with increasing frequencies. However, higher deviations in some intermediate concentration range suggest the existence of strong interaction between, DBP and non polar solvent.

References

[1] J.D Pandey and A.K Shukla, *J. Pure Appl. Ultrason*. 15537 (1993).
[2] Riyazudden and Nurul Islam, J *Pure Appl. Ultrason*. 1916 (1997).
[3] N. Mohanty and R. Paikaray, *Res. J. Chem. Sci*.,3(5), 71, (2013).
[4] S. K. Das, V. Chakravorthy and B. B. Swain, *Acoust., Lett*, 19, 142. (1996)
[5] R. Kumar, S. Jayakumar and V. Kannappan, *Ind. J Pure and Appl. Phys*, .46,169, (2008).
[6] Ashok Kumar Dash and Rita Paikaray, *Res. J. of Phys. Sci*., 1(3), 1, (2013).
[7] S. Thirumaran and N. Karthikeyan, *Int. J of Chem. Res.*, 3(30), 83, (2011).
[8] C. S. Adgaonkar and Agnihotri, *Ultrason*. 27, 248, (1989).
[9] Acharya. S, Paikaray R and Mohanty G C, Indian J Pure and Appl. Phys 41(2003).
[10] G. Nath and R. Paikaray, *Ultra science*, 21(2), 333, (2009).
[11] R Paikaray and N Mohanty, *Journal of Acoustical Society of India*, 37, 70, (2010).