

# A Comparative Study of Binary Mixture of di-n - Butyl Phthalate (DBP) with Polar and Non Polar Liquid

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**Abstract:** A comparative study of binary mixture of Di-n-butyl phthalate (DBP) with polar liquid (aniline, nitrobenzene) and a non polar liquid (benzene, toluene) is carried out at 1MHz frequency and temperature 308K. The ultrasonic velocity (U) in the binary mixture is measured by using ultrasonic interferometric method as a function of concentration and frequency. The experimental measured values of density ( $\rho$ ) and ultrasonic velocity(U) of the binary mixture has been used to compute the different acoustic parameters like isentropic compressibility ( $\beta$ ) intermolecular free length ( $L_f$ ), acoustic impedance (Z) etc. and their excess values. These acoustic parameters and their excess values are used to access and explain the nature and strength of molecular interactions present in the liquid mixture.

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

## 1. Introduction

Ultrasonic velocity measurements have been extensively applied in chemical and industrial processes to assess the nature and strength of molecular interaction in the liquid mixtures. The thermodynamic study of binary mixture in varying composition and environments provides opportunities for the continued adjustment of observable properties and prepares the experimental background for optimizing the solvent choice in manifold application[1-4].

In the present investigation a comparative study of four binary mixtures of Di-n-butyl phthalate (DBP) with polar liquid (aniline, nitrobenzene) and a non polar liquid (benzene, toluene) are carried out at frequency 1 MHz and temperature 308K. Different acoustical parameters such as acoustic impedance, compressibility, free length and their excess functions, interaction parameter of the above said four systems are calculated using the measured ultrasonic velocity and the density of the mixture. These parameters are used to study the nature of interactions occurring in the mixtures at constant frequency and temperature. Further these parameters are compared and their relative merits and applicability are discussed.

A comparative study may throw light on the nature of interaction between polar and polar components and polar and nonpolar components[5-8]. These studies have extensive applications in industries, engineering, medical and almost all other fields. Ultrasonic investigation of liquid mixture consisting of Di-n-butyl phthalate ( $C_{16}H_{22}O_4$ ) (DBP) is an odourless, colourless, polar and viscous liquid 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, and perfume solvent, fixative, antifoam, mosquito repellent etc. and above all it is used as a rocket fuel.

## 2. Material and Methods

The mixtures of DBP with toluene, benzene, aniline and nitrobenzene were prepared by mixing the calculated values. The mass measurement was made using an electronic balance. The accuracy of density measurement is 0.5%. The velocity of sound was measured by using interferometer at 1MHz (Model MS 82, Mittal enterprise, India) at constant temperature 308K which was controlled by using temperature bath jacket with an accuracy of 0.01K. The following relations are used to compute different parameters in the binary liquid mixture[9].

- (i) The acoustic impedance (Z) is given as

$$Z = \rho * U \quad (1)$$

Where U and  $\rho$  are the ultrasonic velocity and density respectively.

- (ii) The adiabatic compressibility ( $\beta$ ) is obtained from equation

$$\beta = 1/\rho U^2 \quad (2)$$

- (iii) Intermolecular free length( $L_f$ ) was calculated by the formula

$$L_f = K \beta^{1/2} \quad (3)$$

Where K is Jacobson's constant and it is temperature dependent. .

- (iv) Interaction parameter ( $\chi$ ) is given by

$$\chi = (U_{exp}/U_{ideal})^2 - 1 \quad (4)$$

The excess values have been calculated using the following relation

$$A^E = A_{exp} - (X_1 A_1 + X_2 A_2) \quad (5)$$

Where  $X_1$  and  $X_2$  are mole fractions of DBP and component liquid respectively.

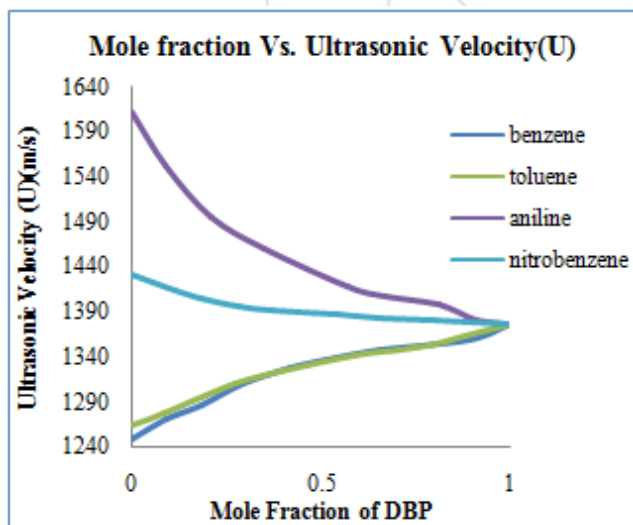
## 3. Result and Discussion

DBP is a polar liquid and hence in pure DBP there are usual dispersive interactions as well as dipole-dipole interaction between the DBP molecules. By adding polar and nonpolar liquid will primarily disrupt the dipolar interaction of the

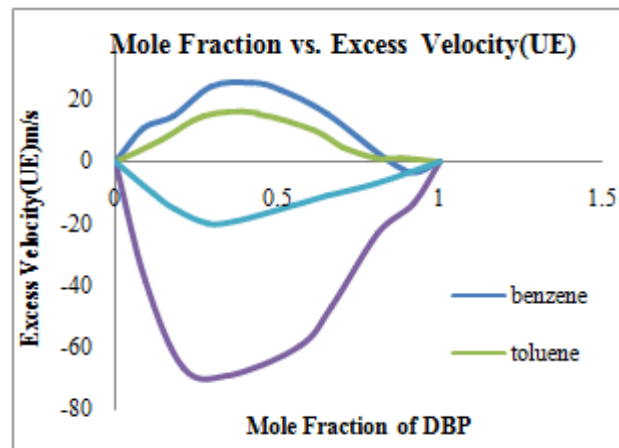
DBP component and the strength of interaction. DBP being a polar liquid interacts with above said polar and non polar liquids and all these components have extensive applications in various fields. The results are discussed comparatively with interpretation invoking the intermolecular interactions[10-13].

The variations of ultrasonic velocity with mole fractions of DBP at 308K and 1MHz frequency for above said four systems are shown in fig-1. The variations of velocities appears to follow a regular trend in case of all systems and it is observed that DBP with nonpolar liquids show an increasing trend with increase in mole fractions of DBP whereas DBP with polar liquids show an opposite trend. The rate of decrease is more in case of mixture of DBP with aniline than nitrobenzene but the rate of increase in velocity is nearly same for the mixture of DBP with benzene and toluene. Decrease in velocity in the mixture of polar and non polar liquid is perhaps due to structural changes in the mixture resulting weakening of intermolecular forces. Hence, DBP with polar liquids have weak intermolecular interactions whereas DBP with nonpolar liquids have strong interactions.

The excess velocities for the four different systems at 1MHz are plotted in the fig-2. It is observed that excess velocity of DBP with benzene and toluene are positive and negative for DBP with aniline and nitrobenzene. The positive excess velocity indicates the molecular association which leads to strong interaction of DBP with nonpolar liquids whereas negative excess velocity is due to molecular dissociation between DBP with polar liquids.

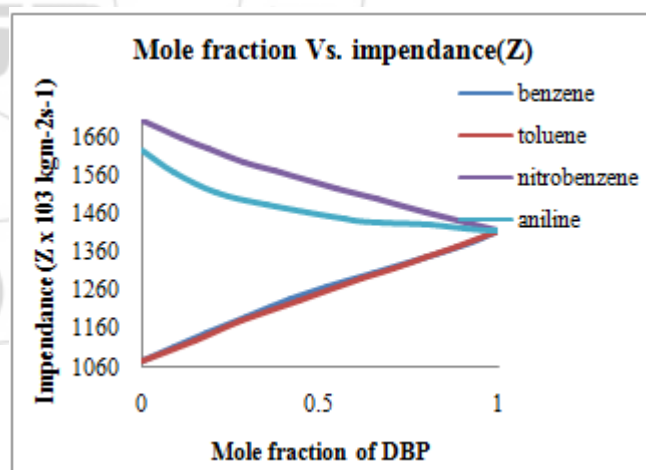


**Figure 1:** Ultrasonic Velocity vs. Mole fractions of DBP for different liquid mixtures



**Figure 2:** Excess Velocity vs. Mole fractions of DBP for different liquid mixture

The acoustic impedance and their excess values of the four systems at 308K and 1MHz are presented in figs-3 and 4. It is observed that the variation of impedance have similar trend as that of velocity. The excess values of impedance indicate the existence of more than one type of interaction in the binary liquid mixtures[9-13]. Acoustic impedance which depend on the molecular packing of the systems shows that excess acoustic impedance is positive for the binary mixture of DBP with nonpolar liquids while negative deviations have been observed in DBP with polar liquids. This indicates the presence of a strong interaction due to dipole-induced dipole interactions in DBP + nonpolar liquids and weak interactions due to dispersive forces which dominant over dipole-dipole interaction between the unlike molecules in DBP + polar liquids.



**Figure 3:** Impedance vs. Mole fractions of DBP for different liquid mixture

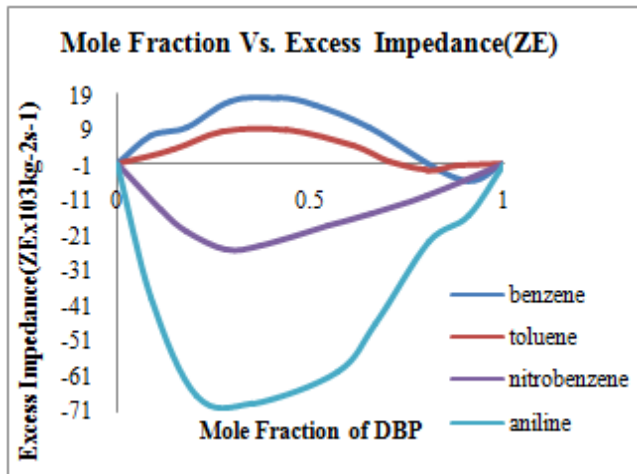


Figure 4: Excess Impedance vs. Mole fractions of DBP for different liquid mixture

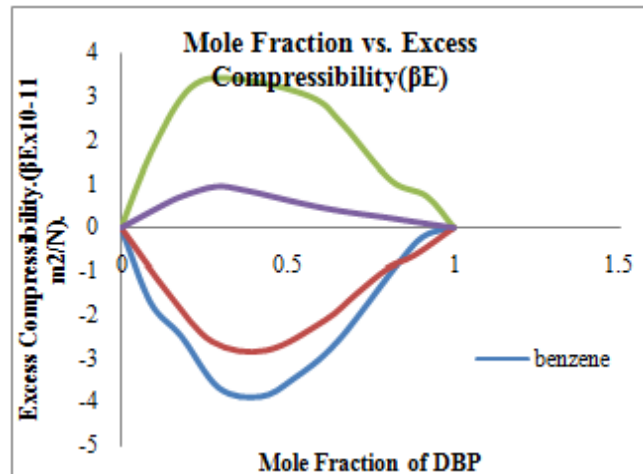


Figure 6: Excess Compressibility vs. Mole fractions of DBP for different liquid mixture

The isentropic compressibility of the mixtures are presented in fig-5 which shows decreasing trend of compressibility with mole fraction of polar and nonpolar liquid mixture such as DBP with benzene and toluene. This suggests strong interaction between DBP and nonpolar liquids. The reverse trend is observed in the binary mixture of DBP with polar liquids. Increasing trend of compressibility is a tendency towards less ordering resulting decrease in ultrasonic velocity which is observed in the present case. This also indicates the molecules of the liquid are loosely packed. The strength of interaction between unlike molecules can be well studied from the excess compressibility. The excess values of the compressibility are presented in fig-6.

The excess compressibility is found to be negative indicating strong intermolecular interaction in the liquid mixture of DBP with benzene and toluene which may be attributed due to dipole-induced dipole interaction. Negative excess compressibility is also due to closed packed molecules of the binary mixture indicating the existence of molecular association. It is also observed that DBP with benzene has maximum negative excess values followed by toluene. Positive excess compressibility is observed in the system of DBP with aniline and nitrobenzene. Positive excess compressibility indicates weak interaction due to dispersive forces and dissociation of molecules in the liquid mixture.

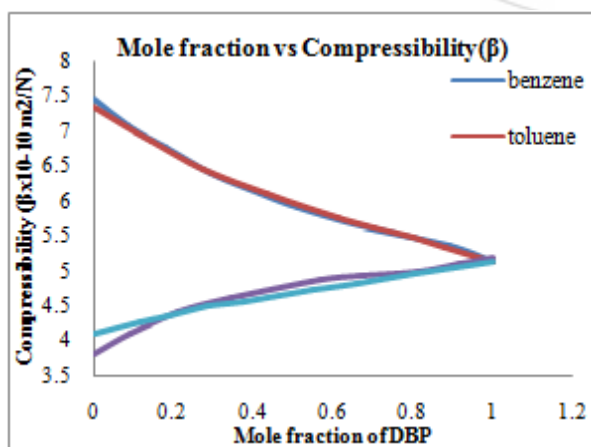


Figure 5: Compressibility vs. Mole fractions of DBP for different liquid mixture

Comparisons of intermolecular free length of different liquid mixture is presented in the fig-7. The ultrasonic velocity in a mixture is mainly influenced by the intermolecular free length between the surfaces of the molecules. Variation of intermolecular free length with mole fraction of DBP is in an increasing trend for the liquid mixture of DBP with aniline and nitrobenzene while shows a decreasing trend for the liquid mixture of DBP with benzene, toluene. This type of variation may be due to different types of packing of the component molecules of the mixture. Loose packing of molecules leads to increase in free length which is attributed as weak molecular interaction. Free length decreases for closely packed component molecules of the mixture which may be due the strong interaction between the polar (DBP) and nonpolar (benzene, toluene) molecules of the binary mixture.

The excess intermolecular free length of different liquid mixtures are presented in fig- 8. The excess intermolecular free length is negative for DBP with benzene and toluene mixture where as it is positive for DBP with aniline and nitrobenzene. The negative contributions of the free length indicate the presence of strong intermolecular interaction between unlike molecules and the positive contributions may be due to the breaking of the self-associated structures of DBP.

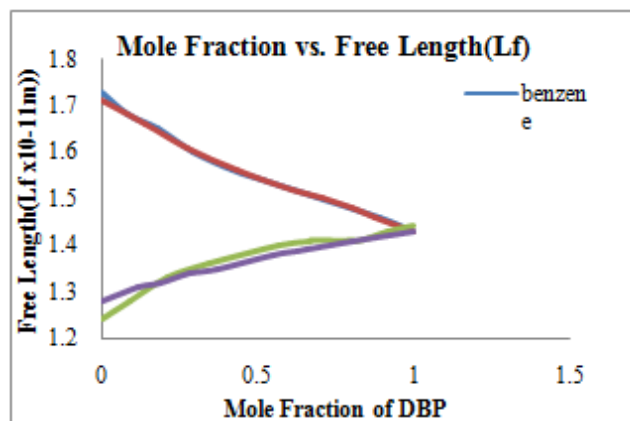


Figure 7: Intermolecular Free Length vs. Mole fractions of DBP for different liquid mixture



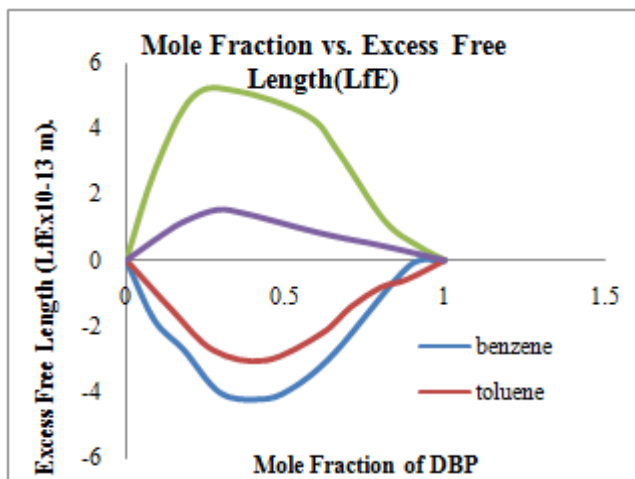


Figure 8: Excess Intermolecular Free Length vs. Mole fractions of DBP for different liquid mixture

This result is supported by excess values of velocity, impedance and compressibility. The negative intermolecular free length is maximum in case of binary mixture of DBP with benzene followed by toluene. The weakest interactions are observed in the binary mixture of DBP and aniline and then DBP with nitrobenzene.

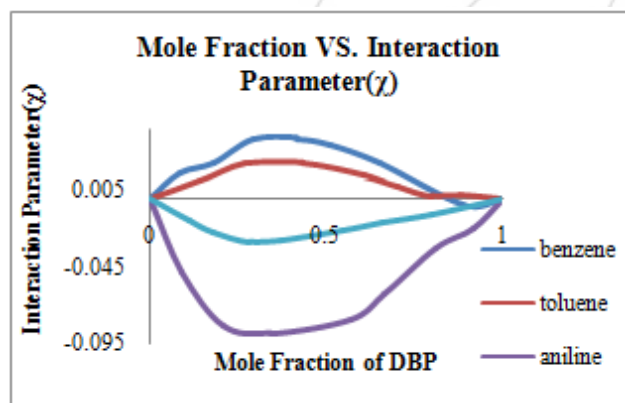


Figure 9: Interaction Parameter( $\gamma$ ) vs. Mole fractions of DBP for different liquid mixture

The variation of interaction parameter of the component molecules for different binary mixtures are presented in the fig- 9. It is observed that DBP with benzene and toluene gives the positive values confirming the strong interaction between the unlike molecules of the mixture as observed in other excess parameters[14-16]. DBP with aniline and nitrobenzene show negative trend indicating existence of weak interaction between the component molecules. Strong interaction is observed between DBP with benzene followed by DBP with toluene.

#### 4. Conclusion

Comparing and analyzing all the values of ultrasonic velocity, impedance, compressibility and intermolecular free length and their excess values for binary mixtures at 1MHz frequency and 308K temperature, it is found that DBP has stronger interaction with nonpolar liquids (benzene and toluene) and weak interactions with polar liquids (aniline and nitrobenzene). The strong interactions of DBP with nonpolar liquids are due to dipole-induced dipole

interactions between unlike molecules. The weak interactions are due to predominance of dispersive force over dipole-dipole interaction. Molecular association or close packing of molecules is operative in the liquid mixture of DBP with nonpolar liquids while dissociation or loose packing of molecules is observed in the liquid mixture of DBP with polar liquids. Interaction is relatively stronger in DBP + benzene followed by DBP + toluene, DBP + nitrobenzene, DBP + aniline.

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