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RESEARCH ARTICLE

Ultrasonic Study of Binary Mixture of Acetone with Bromobenzene and Chlorobenzene at Different Frequencies

G. NATH

Department of Physics, Veer Surendra Sai University of Technology (VSSUT), Odisha, India
ganesh_nath99@yahoo.co.in

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Abstract: This paper aims to portray the nature and extent of interaction in the binary mixture of acetone with bromobenzene and chlorobenzene by computing the various acoustic parameters such as acoustic impedance (Z), isentropic compressibility (β), intermolecular free length (L_f) and their excess values at different frequencies (1 MHz, 3 MHz and 5 MHz) using a multi frequency ultrasonic interferometer over the entire range of mole fraction at temperature 303.16 K. The experimental data for sound velocity (C) and density (ρ) of the mixture have been used to compute these parameters. The variations of sound speed with frequency plays the key role to execute the variation in these parameters which is explained in terms of different intermolecular interactions present in the binary mixture. The extent of interactions existing between component molecules has been found out. In acetone-bromobenzene system the more negative values of different excess parameter suggest that the interaction between acetone-bromobenzene is more as compare to acetone-chlorobenzene system. Further a comparative study for the above acoustical parameters between two mono substituted benzene in presence of acetone at different frequencies were discussed in terms of molecular interactions.

Keywords: Ultrasonic velocity, Isentropic compressibility, Intermolecular free length, Acoustic impedance

Introduction

The study of pure liquids and their properties can not be altered continuously within a reasonable range by varying the concentration till an optimum value of some desired parameter is attained. This is only possible by considering the liquid mixtures and solutions which find direct applications in many chemical industries and technological processes. Further, such studies as a function of concentration are useful in understanding the intermolecular interactions between the component molecules and more insight into the structure and bonding of associated molecular complexes and other molecular processes. Since ultrasonic velocity is fundamentally related to the binding forces between the constituents of the medium[1] so it is highly sensitive to the structure and interactions present in the liquid system. The measurement of ultrasonic velocity of sound in liquids enables determination

of some useful acoustic and thermodynamic parameters that are found to be very sensitive to molecular interactions. Hence, these measurements are useful to study the strength of molecular interactions in liquid mixtures. Again ultrasonic investigation of liquid mixtures consisting polar and polar components is of considerable importance in understanding intermolecular interaction between the component molecules and they find application in several industrial and technological processes. As the excess thermodynamic functions are sensitively dependent on different in intermolecular forces and size of the molecules, so these properties have been widely used to study the intermolecular interactions between the various species present in the liquid mixtures. Increasing use of acetone, bromobenzene and chorobenzene in many industrial processes have greatly stimulated the need for extensive information on the acoustic and transport properties of these liquids and their mixtures. Commercial use of acetone includes as an important solvent in different chemical industries, an automotive fuel additive to increase the engine life and improvement in fuel economy. It is also used in mining industries for safely store and transport the highly explosive and flammable acetylene. Toluene is used as a common solvent, chemical reactant, fullerene indicator and raw material for toluene di-isocyanate and TNT. It is also used as a carbon source for making multi wall carbon nano tubes and in many biochemical experiments. In addition with the above liquids xylene is also used as raw material in the production of monomer, good cleaning agent for silicon wafers and steel, as a feedstock in the production of petrol .It is also found in small proportions in gasoline and jet fuel. These liquid mixtures are of interest to many chemical industries for preparation of many chemical products like polycarbonate, polyurethanes, cement industry, fuel industry used in internal combustion engines particularly by the Honda team. In preparation of multi wall carbon nanotube, as a coolant for good heat transfer in nuclear reactor acetone and toluene used in a suitable amount. Although several investigation were carried out in liquid mixtures having acetone or toluene or xylene as one of the components, for a fixed or different temperature at constant frequency but no literature was found for binary mixture of such liquid at different frequencies. As variation of frequency affects different acoustic parameter of binary and ternary liquid mixture so authors have put interest to carry out the investigation process for binary mixture of such liquids. The present paper deals with the study of ultrasonic velocity, acoustic impedance, isentropic compressibility, intermolecular free length and their excess values of acetone with toluene and xylene at three different frequencies. An attempt has been made to compare the extent of interactions between toluene and xylene in presence of acetone and effect of frequency on these parameters as well as on the intermolecular interaction has also been explained. The utility of acetone in different chemical extraction industries, solvent extraction in nuclear energy industries and practical applications like in paints and varnish *etc*. encouraged us to initiate the systematic studies of their physicochemical properties in different polar liquids like bromobenzene (B.B) and chlorobenzene (C.B). Ultrasonic velocity measurement is a powerful tool to study the thermodynamic properties and predict the intermolecular interaction of binary mixtures. The ultrasonic velocity is one of those physical properties that help in understanding the nature of liquid state. Using the measured values of ultrasonic velocity (C) and density (ρ), the thermodynamic properties such as intermolecular free length (L_f), isentropic compressibility (β) and acoustic impedance (Z) in binary mixtures of acetone with bromobenzene and chlorobenzene have been measured throughout the composition range of acetone. The variation of ultrasonic velocity with different frequencies and hence the variation of intermolecular free length with ultrasonic velocity at a particular temperature and concentration of binary mixtures of different polar liquids with acetone creates more interest in studying their interactions and molecular environment of the binary

mixture. Therefore, in the present investigation the study of ultrasonic velocity with mole fraction of acetone at different frequencies (1MHz, 3MHz and 5MHz) at temperature of 303.16 K has been undertaken.

Theory

The experimental measured values of ultrasonic velocity and density are used to compute acoustic parameters such as intermolecular free length (L_f), isentropic compressibility (β), acoustic impedance (Z) and their excess values[1]. The above acoustic parameters are determined with the help of the following relationship.

$$\text{Isentropic compressibility, } \beta = \frac{1}{\rho C^2} \quad (1)$$

$$\text{Intermolecular free length, } L_f = K\beta^{1/2} \quad (2)$$

$$\text{Acoustic impedance } Z = \rho C \quad (3)$$

and their excess values are calculated as

$$\beta^E = \beta_n - (X_A\beta_A + X_B\beta_B) \quad (4)$$

$$\text{and} \qquad Z^E = Z_n - (X_AZ_A + X_BZ_B) \quad (5)$$

Where X_A, X_B, β_A, β_B, β_n, Z_A, Z_B and Z_n are mole fraction, isentropic compressibility and acoustic impedance of B.B/C.B, acetone and individual polar liquid (B.B, C.B.) with acetone respectively.

Experimental

In the present study the chemicals used were of analytical grade (E-Merck) purified by standard procedure[2-4] and redistilled before use. Density was determined with a Pyknometer of 25 cm^3 capacity, calibrated at 303.16 K with de-ionized double distilled water. At a fixed temperature, the density was determined with an error of one in 10^4. Ultrasonic velocity was measured by a single crystal variable path interferometer operating at different frequencies of 1MHz, 3MHz and 5MHz. Circulating water from thermostatically regulated bath around the sample holder with double wall, which maintains the temperature of the liquid constant with a precision of $\pm$0.1 ^oC. Binary mixtures of acetone were prepared with bromobenzene and chlorobenzene with varying fraction of acetone.

Results and Discussion

Experimentally determined density and ultrasonic velocity were used to calculate isentropic compressibility (β), intermolecular free length (L_f), acoustic impedance (Z) and excess values of β^E and Z^E using the standard relations[5] with accuracy up to third decimal digit. The variations of these thermodynamic parameters with entire concentration range of acetone at different frequencies are displayed graphically in Figure 1 to 4. The Figure 1 shows the variation of ultrasonic velocity against mole fraction of acetone which is not linear. It is seen that the ultrasonic velocity decreases or increases with mole fraction of acetone, depending on the ultrasonic velocity value of second component. This suggests that dipole-induced dipole attraction is stronger than induced dipole-induced dipole attraction where linear plots are normally obtained. In low concentration around 43 mole% of acetone the ultrasonic velocity decreases gradually in both bromobenzene and chlorobenzene demonstrating the non-linear trends. Around 50-76 mole% of acetone the variation in ultrasonic velocity is very low for which in this region the profiles are linear in nature. But when the concentration of acetone is above 80 mole% the profiles are further demonstrates increasing trend. At frequency range

1 MHz the interaction between acetone-bromobenzene and acetone-chlorobenzene is slow for which the ultrasonic velocity is low. The difference in ultrasonic velocity in mixture of acetone + B.B. and acetone + C.B. can be interpreted taking account of electro negativity of bromine and chlorine. As the electro negativity and hence the polarity of chlorine (3.16) is higher than bromine (2.96), so the molecules of bromobenzene are more free to move as compared to chlorobenzene. Hence the ultrasonic velocity in pure bromobenzene is higher than chlorobenzene in their rich regions. As the concentration of acetone goes on increasing gradually, the interaction between acetone + B.B. and acetone + C.B. increases due to formation of α-multimers in acetone for which there is a very less difference in ultrasonic velocity. Again in acetone rich region as the interaction between solute (acetone) and solvent (B.B., C.B.) is less so the molecules of acetone are free from mutual interaction and hence moves with high velocity. Further when frequency changes 1 MHz to 5 MHz, the interaction between solvent and solute is negligible and the ultrasonic velocity increases demonstrating the similar trends as observed at low frequency range 1 MHz.

The Figure 2 shows the variation of intermolecular free length with mole fraction of acetone. It is clear that with increase in concentration of acetone the intermolecular free length initially increases both for B.B and C.B and then decreases at the high concentration range around 90 mole% of acetone.

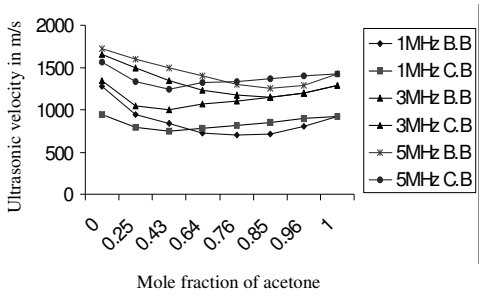

Figure 1. Schematic variation of ultrasonic velocity with mole fraction of acetone

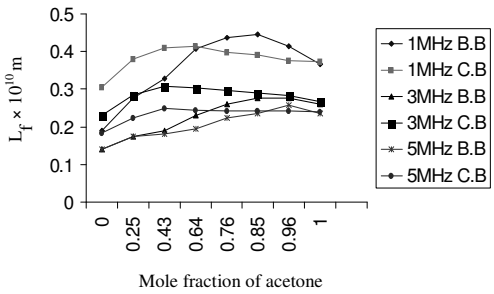

Figure 2. Schematic variation of intermolecular free length with mole fraction of acetone

Considering the frequency variation, it is to be noted that at low frequency range (1 MHz) C.B has maximum value of intermolecular free length as compared to B.B. in the same concentration range. This is due to fact that in the mixture of acetone and C.B, the electro negativity in oxygen-chlorine is negligible and hence interaction is very small as compared to that of interaction between oxygen-bromine in acetone and B.B mixture. When the concentration of acetone increases the polarity of B.B and C.B decreases, hence the intermolecular free length decreases as the interaction increases between the component molecules. With increase in frequency, as the polarity is no longer observed, the moment of the molecule is due to intermolecular gap. So the intermolecular free length is less in high frequency range and shows a small variation in trend (3 MHz). In high frequency range (5 MHz) the interaction is very negligible, so the molecules are able to move freely for which the intermolecular free length sharply increases up to 85-90 mole% of acetone and then decreases in pure acetone state as the interaction between the acetone molecules is more. Figure 3 demonstrates the excess values of isentropic compressibility (β^E) for the binary mixture of acetone and bromobenzene and acetone and chlorobenzene with mole fraction of acetone at different frequencies.

From the plots for β^E it is clear that, the excess values of β^E decreases negatively in magnitude and approach a minimum at around 70 mole % of acetone for B.B and 50 mole% of acetone for C.B in low frequency range (1 MHz) which suggest that maximum structural changes takes place in this region of solvent mixture. In both mono substituted benzene, the drops are almost at the same rate with sharp fall in acetone deficient region and slow fall in acetone rich region. It is also to be noted that in low frequency range (1 MHz) for B.B, the β^E value has more negative value as compared to C.B. Of the two polar solvents used here, the chlorobenzene is more reactive because the chlorine atom is bonded with Sp^3 hybridized carbon atom and consequently can be removed easily. So the rate of reaction with chlorobenzene is faster. On the other hand, bromobenzene is less reactive because of its double bond character between carbon and bromine atom[5]. This slow reaction in case of B.B may also be attributed to its being heavier. Thus the molecular interaction is likely to be more affected. Again with increase in frequency (3 MHz and 5 MHz) the molecule vibrates more rapidly, so that there will be no longer interaction among the molecules. Hence they will acquire maximum volume and compressibility will be more for which the profiles are close to each other in 3 MHz frequency in the concentration range from 50 to 98% of mole fraction of acetone. Further increase in frequency (5 MHz) the molecules will take a little time to interact with molecules of other polar liquids and move very rapidly. As a consequence they occupy a large volume and compressibility shows the same trend as shown in the frequency range of 3 MHz. Thus it is found that the value of β^E is greater in magnitude in case of B.B as compared to C.B for every frequency and the dramatic variation of β^E explains the degree of interaction in different components of the molecules[6]. The excess value of acoustic impedance (Z^E) is appreciable negative over the entire composition of acetone for all frequencies as shown in Figure 4.

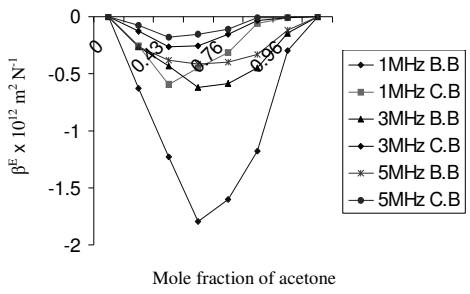

Figure 3. Schematic variation of excess isentropic compressibility with mole fraction of acetone

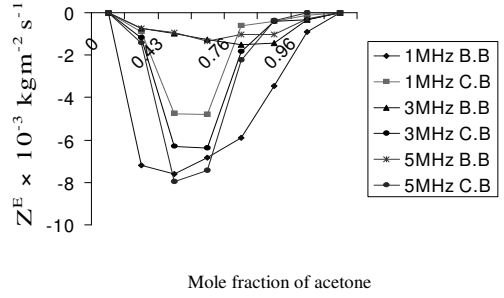

Figure 4. Schematic variation of excess acoustic impedance with mole fraction of acetone

As more than one type of interaction present in a given mixture[7], the increase in mixed interaction like dispersion, *H*-bonding, α-multimer *etc*. increases the acoustic impedance. Dispersion forces make a positive contribution to the excess values while the dipole-dipole interaction makes negative contribution[8]. As the C.B is more electronegative as compared to B.B so the polarity of C.B is also high compared to B.B for which a strong dipole-dipole interaction exists and makes a negative contribution over the entire mole fraction of acetone. Again with the increase in frequency from 1 MHz to 5 MHz as the interaction is less, so the molecule moves with high speed giving a small variation in impedance which is clearly observed from profiles.

Conclusion

Thus it can be concluded that the interaction of acetone with C.B is stronger than the interaction with B.B as is observed in different ultrasonic parameters for different frequencies. Thus it is to be further noted that the frequency plays a vital role in studying the different ultrasonic parameters in different combination of binary mixtures at constant temperature.

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