Ultrasonic Investigation of Intermolecular Interactions in Binary Mixture of Isobutyl Methyl Ketone and Acetone

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Abstract

The density (ρ) and ultrasonic velocity (U) in binary mixture of isobutyl methyl ketone(MIBK) and acetone at constant frequency 2MHz have been measured at 308K. These data have been used to compute adiabatic compressibility (K_s), intermolecular free length (L_f), acoustic impedance (Z), molar volume (V_m), molar sound velocity(R_m), molar compressibility (B), available volume (V_a), Lennard Jones potential repulsive term exponent(n), relative association(R_a), interaction parameter (χ) and excess values of some of the above parameters for the entire range of mole fraction of MIBK and are interpreted to explain intermolecular interactions occurring in the liquid mixture.

Keywords: Molar volume, Lennard Jones potential repulsive term exponent, relative association, interaction parameter, binary mixture

Introduction

The ultrasonic study of liquids is related to the binding forces between atoms or molecules. Ultrasonic velocities have been extensively employed to understand the nature of intermolecular interactions in pure liquids, binary, ternary and quaternary mixtures [1-7].The investigation regarding the study of intermolecular interaction in binary liquid mixture with isobutyle methyle ketone and acetone as the components is of particular interest. MIBK is a flammable liquid with high vapor pressure which is used only with good ventilation. It has both industrial and consumer applications. MIBK does not cause adverse health or environmental effects typically found in the workplace. Acetone is an important solvent used in industries and pharmaceuticals.

Owing to these considerations, an attempt has been taken to explain the molecular interaction in binary liquid mixture of isobutyle methyle ketone and acetone at constant temperature(308K) and frequency 2MHz. Departure from linearity in the velocity versus concentration in liquid mixture is taken as an indication of the existence of intermolecular interactions between different liquid molecules [8-11].

Experimental Method

The 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. Liquid mixtures of different mole fractions were prepared on concentration scale with a precision of 0.0001g using an electronic digital balance. Densities of liquid mixtures were determined by a specific gravity bottle of 10ml capacity. The ultrasonic velocity was measured by a single crystal interferometer (M-82S) with a high degree of accuracy of ± 0.01 m/s operating at constant frequency 2MHz and at constant temperature 308K. An electronically operated constant temperature water bath was used to circulate water through the

double walled measuring cell made up of steel containing the experimental liquid mixture of MIBK and acetone at the desired temperature.

Theory

The ultrasonic parameters such as adiabatic compressibility (K_s), intermolecular free length (L_f), acoustic Impedance (Z), molar volume (V_m) and available volume (V_a) have been calculated using the experimental data from the following relations[12].

$$K_s = (U^2\rho)^{-1} \quad (1)$$

$$L_f = k\,(K_s)^{-1/2} \quad (2)$$

$$Z = \rho U \quad (3)$$

$$V_m = M/\rho \quad (4)$$

$$V_a = (M/\rho)\,(1-U/U_\infty) \quad (5)$$

Where k is a temperature dependent constant, M is the molecular mass of the liquid mixture and U_∞=1600 m/s.

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

$$A^E = A_{exp} - (X_1A_1 + X_2A_2) \quad (6)$$

Where X_1, and X_2 are mole fractions of MIBK and acetone respectively and A is any acoustical parameter.

Molar sound velocity(R), molar compressibility (B), Lenard Jones potential repulsive term exponent (n), relative association (R_A) and interaction parameter (χ) have been calculated using following relations [13-14].

$$R = (M/\rho)\,U^{1/3} \quad (7)$$

$$B = (M/\rho)\,(K_s)^{-1/7} \quad (8)$$

$$n = (6\,V_m / V_a) - 13 \quad (9)$$

$$R_a = (\rho/\rho_0)\,(U_0/U) \quad (10)$$

$$\chi = (U/U_{ideal})^2 - 1 \quad (11)$$

Where ρ_0 and U_0 are density and ultrasonic velocity of MIBK respectively.

The ideal mixing velocity U_{ideal} is given by

$$U_{ideal} = X_1U_1+X_2U_2 \quad (12)$$

Lenard-Jones potential $\varphi(r)$ is given by the relation .

$$\varphi(r) = -Ar^{-6} + Dr^{-n} \quad (13)$$

Where r is intermolecular distance, A and D are constants.

Results and Discussion

The experimental values of density and ultrasonic velocity at 308K for pure liquids and binary liquid mixture were used to calculate various acoustical parameters. Figs -1 and 2 show that density ρ and ultrasonic velocity U increase with the increase in mole fraction of MIBK. The increase in ultrasonic velocity with the increase in concentration of MIBK at a particular frequency may be due to the structural changes occurring in the binary mixture resulting the increase in intermolecular forces.

The variation of excess velocity with the increase in mole fraction of MIBK is shown in fig-3. The excess velocity(U^E) shows positive deviation for the entire range of mole fraction of MIBK. The positive deviation in excess velocity indicates the presence of dipole-dipole interaction in the entire range of mole fraction of MIBK

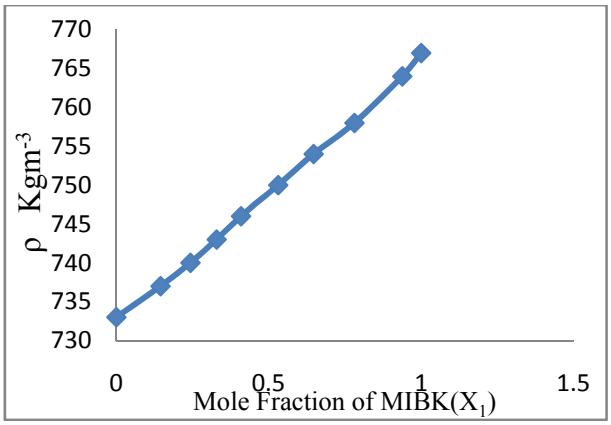

Fig-1: Variation of ρ Versus X1

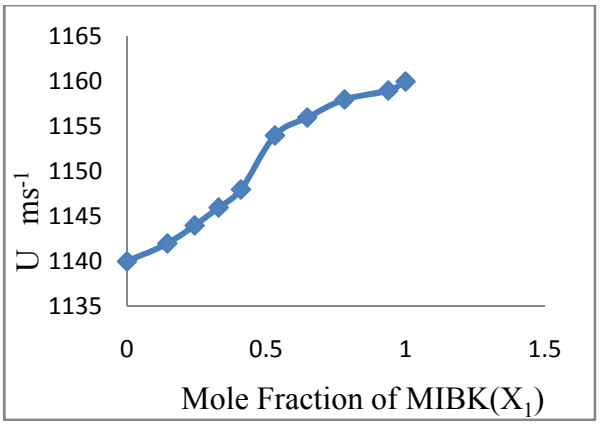

Fig-2: Variation of U Versus X1

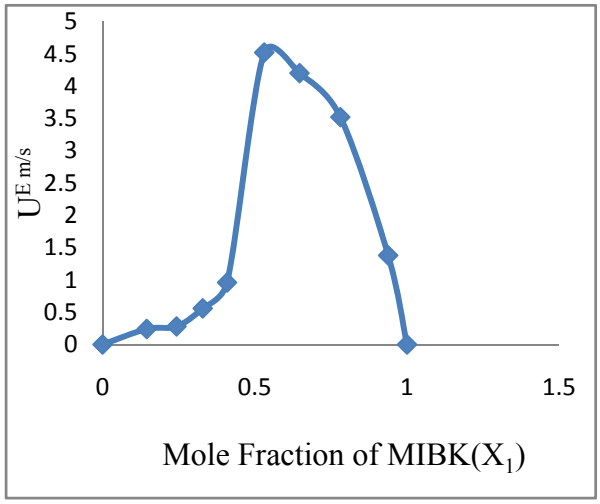

Fig-3: Variation of U^E Versus X1

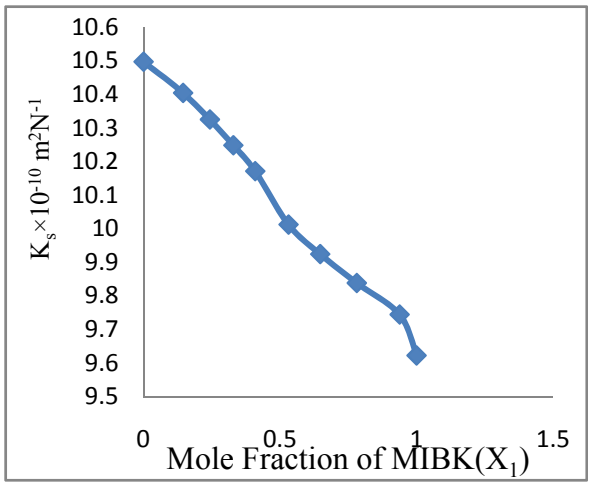

Fig-4: Variation of K_s Versus X1

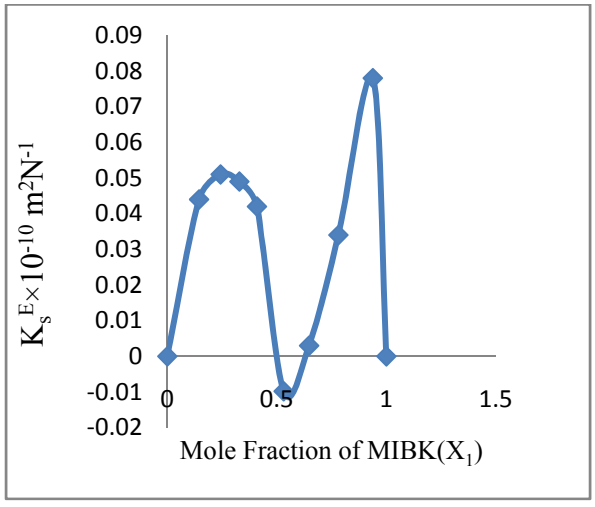

Fig-5: Variation of K_s^EVersus X1

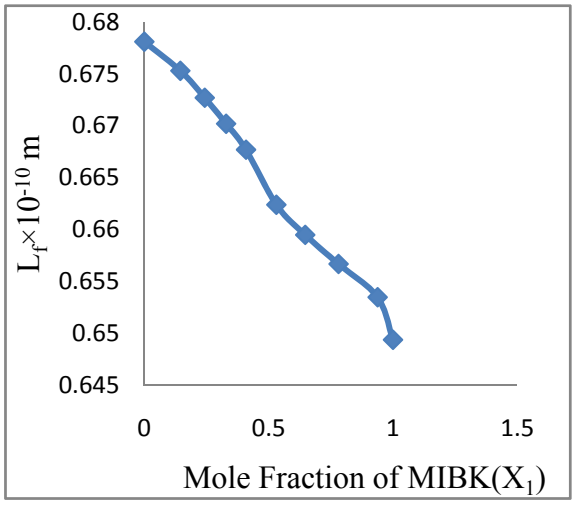

Fig-6: Variation of L_f Versus X1

The variations of adiabatic compressibility K_s and excess adiabatic compressibility with the increase in mole fraction of MIBK are shown graphically in figs -4 and 5 respectively. The adiabatic compressibility of the MIBK and acetone mixture decreases with the increase in mole fraction of MIBK. The decrease in adiabatic compressibility exhibits the presence of molecular interaction inside the liquid mixtures and the molecules are closer to each other[15]. The positive values of K_s^E for the lower and higher MIBK concentration regions predict the existence of dispersion interactions in the binary system. The negative values of K_s^E for the equimolar MIBK concentration region predict the existence of strong molecular interactions due to charge transfer and formation of hydrogen bond, dipole-dipole interactions in the binary system.

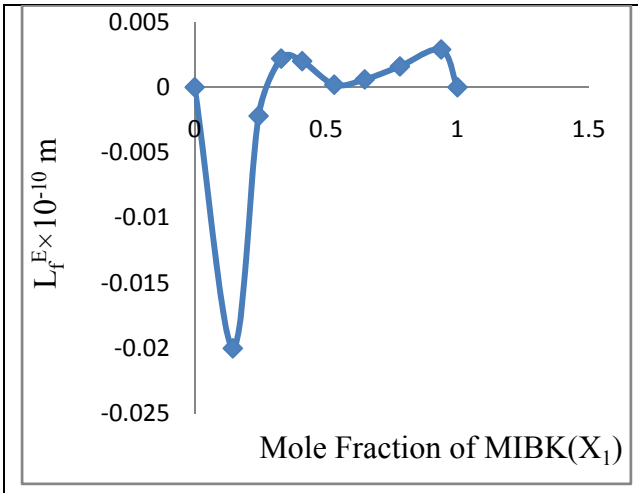

Fig-7: Variation of L_f^E Versus X1

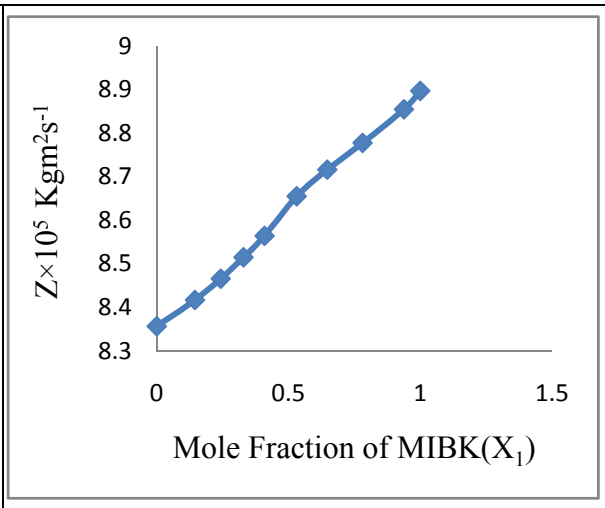

Fig-8: Variation of Z Versus X1

The experimental data of inter molecular free length and excess intermolecular free length are graphically presented in figs-6 and 7 respectively. These are in agreement with the Eyring Kincaid model for sound propagation [16]. According to which the ultrasonic velocity will increase with the decrease in intermolecular free length and vice versa. Hence intermolecular free length is a predominating factor for deciding the nature of variation in ultrasonic parameters in the liquid system. The decrease in intermolecular free length also causes increase in density and acoustic impedance.

The positive values of excess free length for higher MIBK concentration regions are due to the dispersive forces. The negative excess values of free length L_f^E for the lower MIBK concentration region predict the existence of strong molecular interactions in the binary liquid mixture due to charge transfer and formation of hydrogen bond.

It is observed from the profile that acoustic impedance of the system increases with the increase in concentration of MIBK as shown in fig-8. It exhibits the same trend as that of velocity graph indicating the presence of molecular interaction of unlike molecules. Fig-9 shows that Z^E is negative for the lower composition range of MIBK indicating the presence dispersive forces between unlike molecules and positive for the higher composition range of MIBK indicating the presence of dipole-dipole interactions in the binary liquid mixture.

The compactness and strength of bonding between the molecules of the liquid mixture are measured directly by the available volume[17]. Fig - 10 shows that the values of available volume V_a increases with the increase in mole fraction of MIBK. The values of excess available volume V_a^E are

positive for the whole concentration range of MIBK as shown in fig -11 indicating the presence of dispersive forces in the binary liquid mixture[18].

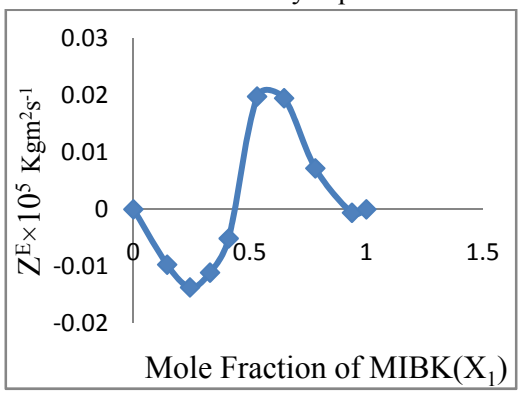

Fig-9: Variation of Z^E Versus X

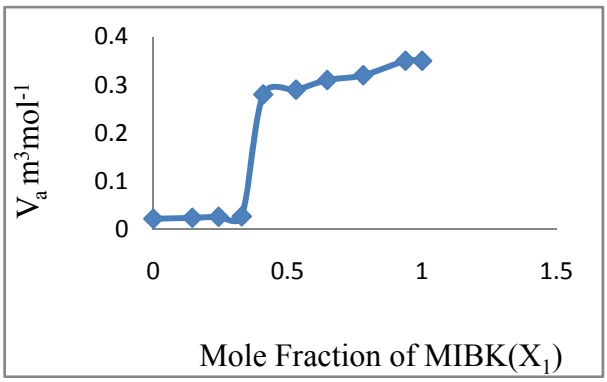

Fig-10: Variation of V_a Versus X1

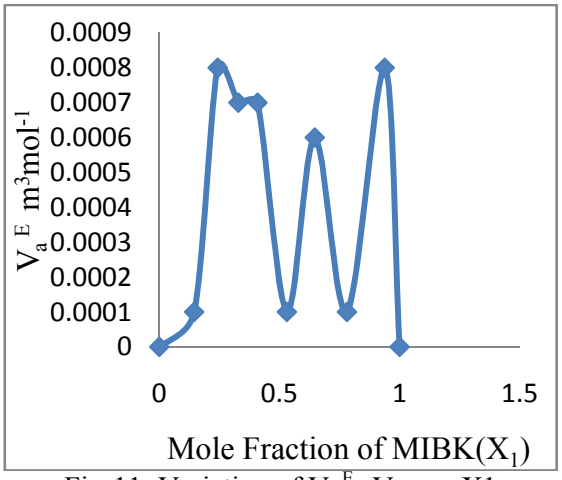

Fig-11: Variation of V_a^E Versus X1

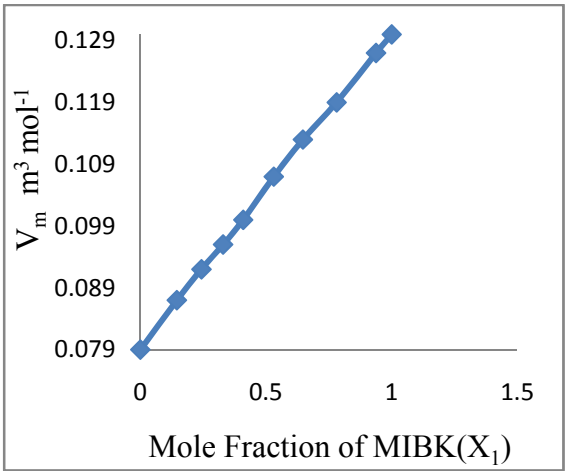

Fig-12: Variation of V_m Versus X1

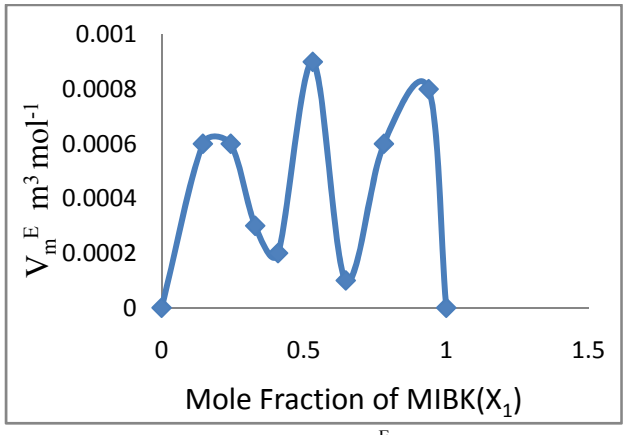

Fig-13: Variation of V_m^E Versus X1

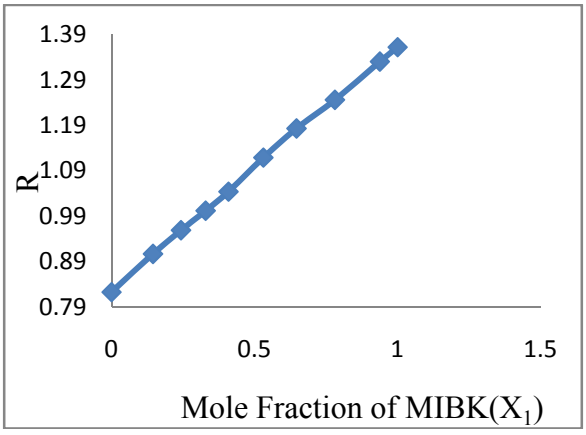

Fig-14: Variation of R Versus X1

Molar volume of the mixture have an increasing trend with mole fraction of MIBK and excess molar volume is positive over entire range of mole fraction as shown in figs- 12 and 13 respectively. The positive excess molar volume indicates the expansion of volume and this may be due to relative strength

of dispersive force over dipole-dipole attractive force. Further, expansion in volume may be due to steric hindrance of component molecules, unfavorable geometric fitting and electrostatic repulsion[19].

Molar sound velocity R or Rao's constant is a factor in deciding the molecular association in the liquid mixture. Fig -14 represent the increasing values of R. In the present work, the linear variation of R with mole fraction in MIBK indicates the associative nature of liquid mixture and the absence of complex formation.

Fig -15 shows that the Relative association (R_A) for the mixture of MIBK and acetone increases with the increase in mole fraction of MIBK indicating the presence of molecular interaction between unlike molecules. Further, these results confirm the dipole-dipole interaction between MIBK and acetone.

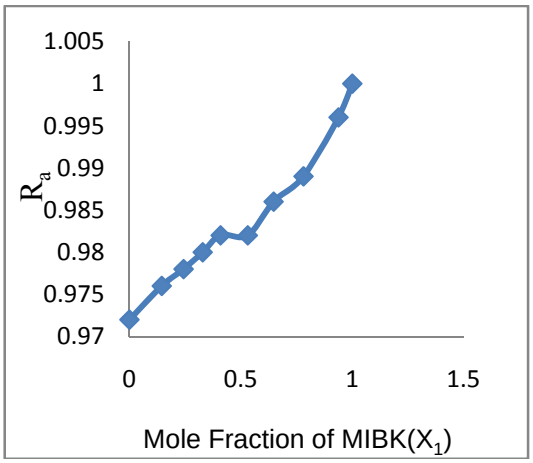

Fig-15 : Variation of R_a Versus X1

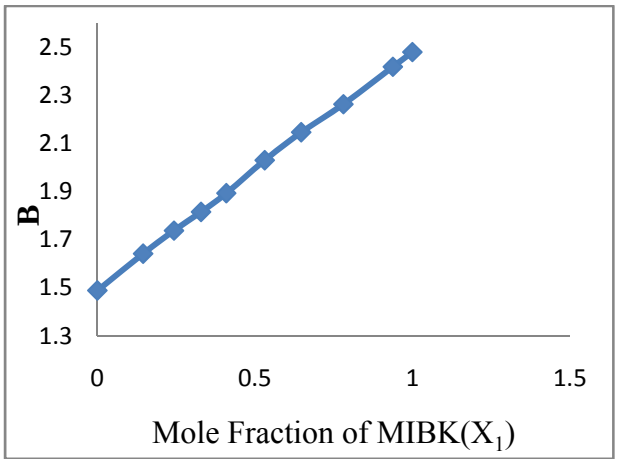

Fig-16: Variation of B Versus X1

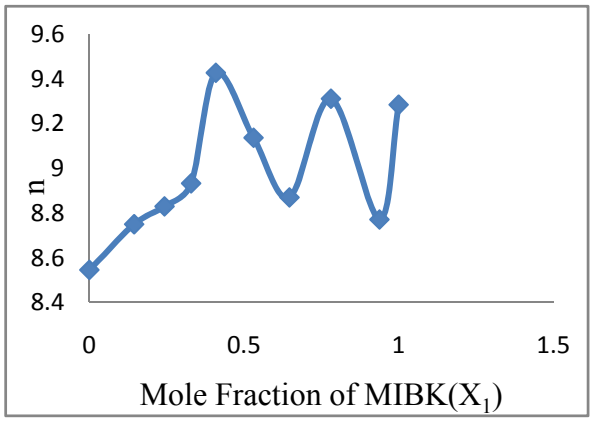

Fig-17: Variation of n Versus X_1

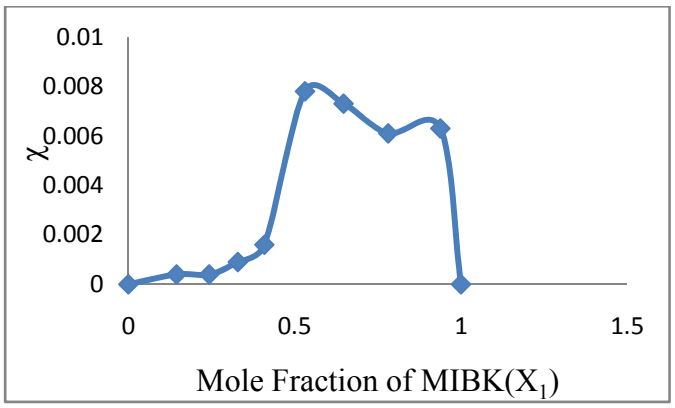

Fig-18: Variation of χ Versus X_1

Fig- 16 shows that the values of Wada's Constant B increase linearly with the increase in mole fraction of MIBK. The linear increase in Wada's Constant indicates the presence of dipole-dipole interactions in the binary liquid mixture without complex formation

The non linear variation of Lenard Jones potential repulsive term exponent n of the mixture with mole fraction of MIBK is shown in fig- 16. The first term of Lenard Jones potential arises from attractive forces while the second term arises from repulsive forces [20]. The increase in n for the lower concentration

of MIBK indicates the dominance of attractive forces over repulsive forces in the binary liquid mixture. However, n shows irregular trend at higher concentration region.

Fig-18 shows that the values of interaction parameter χ are positive for the entire range of mole fraction MIBK which indicates the existence dipole- dipole interactions in the binary liquid mixture.

Conclusion

The ultrasonic velocity, density and other computed parameters which depend on the composition of the liquid mixture indicate the presence of molecular interactions. Deviation of the excess parameters from linearity shows that the interactions are primarily of dipole–dipole type. Expansion in volume of the mixture may be due to steric hindrance of component molecules, unfavorable geometric fitting and electrostatic repulsion. However, the linear variation of Rao's constant and Wada's Constant indicate molecular interaction without complex formation in the liquid mixture of MIBK with acetone.

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