STUDY OF THE MOLECULAR INTERACTION IN TERNARY LIQUID MIXTURES BY ULTRASONIC VELOCITY MEASUREMENT

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ABSTRACT

In recent years there has been considerable advancement in the experimental investigation of thermodynamic properties of liquid mixtures. The ultrasonic velocity, density have been measured for the mixture of esters namely;methyl acetate, ethyl acetate and n-butyl acetate in 1,4 Dioxane with water at 296.15 K.These properties have been adequately applicable to understanding the nature of molecular interaction in ternary liquid mixtures. The experimental data have been used to calculate acoustical parameters namely adiabatic compressibility (β), acoustic impedance (Z) and free length (L_f). The results are interpreted in term of solute solvent interaction in the solution.

Key Words: *Ultrasonic velocity, intermolecular free length, adiabatic compressibility, acoustic impedance, dipole - dipole interaction.*

Introduction

In recent years the measurement of ultrasonic velocity has got great importance in understanding the nature of molecular interaction in pure liquid and liquid mixtures. The ultrasonic velocity measurements are highly sensitive to molecular interaction and can be uses to provide qualitative information about physical nature and strength of molecular interaction in liquidmixyures[Mehata S.et.al.1996 andDewan R.et.al.1991]. Ultrasonic velocity in a liquid is basically related to binding forces between atoms and molecules; it has been successfully employed in understanding the nature of molecular interaction in pure liquids, binary and ternary liquid mixtures[Tabane V.et. al. 1999 and Aswale S.S.et.al.2012] An experimental study carried out by the authors and reported the following parameters value of the ternary mixtures system.

The observation of following liquid system were taken at 296.15 K.

System-I = Methyl acetate + 1, 4 Dioxane + water

System-II = Ethyl acetate + 1, 4 Dioxane + water

System-III = n-Butyl acetate + 1, 4 Dioxane + water

Ester is applicable in different field, such as artificial fruit essences, aroma in enhancers, artificial flavor, vanishing cream,paints, manufacturing of printing ink, perfumes, as plasticizer etc.

Although several investigations [Rajathi K.et.al, 2011 and Harish kumara et. al.2012] were carried out in liquid mixtures having ester as one of the component. A systematic study in a series of ester in ternary liquid has been scarcely reported [Anbarasu S.et. al. 2010]

Materials and Method

Materials: The chemicals used in the present work methyl acetate (99.5%), ethyl acetate (99.8%) n-butyl acetate (98.9%) and 1-4 Dioxane were analR-grade and spectroscopic reagent (SR) grades with minimum assay were obtained from Hi media chemicals without further purification. The densities of pure liquid and the mixtures with literature values are listed in table 1 to 3,

The instrument is calibrated with double distilled water and resultsarecompare with literature value at 298.15 K. [NaikA.B. et. al. Dec. 2009]

Dwg/m3	Lit. value	$U_{.m/s}$	Lit. value
l997	**998[13]**	**1509**	**1507**

Preparation of ternary mixtures:

In all systems the various concentration of the ternary liquid mixtures are prepared in terms of mole fractions.The mole fraction of second component that is 1,4Dioxane (X_2=0.4) was kept fixed,The liquid mixtures were preserved in well stopped conical flasks. After mixing the liquid thoroughly, the flask were kept undisturbed to attain thermal equilibrium

Measurement of ultrasonic velocity:

The different methodsare applicable for the measurement of ultrasonic velocity includes

i) Optical Method ii) Pulse Technique iii)Interferometric Method.

In this investigation the interferometric method has been used.The ultrasonic velocity has been measured by using multi frequency ultrasonic interferometer (Model no. M-81S) Mittal EnterprisesNew Delhi, at frequency 2 MHz with an overall accuracy of ± 3 ms^{-1}. All the measurements were taken at fixed temperature296.15 K.

Apparatus and procedure: Thedensity of pure liquid and liquid mixtures isdetermined using a specific gravity bottle by relative measurement method with an accuracy of ± 0.1mg.All the weighingswere taken on electronics analytical balance(SHIMADZU AY-220).Measurements of ultrasonic velocity (U) and density (ρ) of liquids are useful to determine the thermodynamics and acoustical parameters of the ternary mixtures. This acoustical and thermodynamic property helpsto understand the characteristics of different liquids. The nature of molecular interaction in the liquid can be proved by making use of parameters such as adiabatic compressibility (β) acoustics impedance (z) and free length (L_f). These parameters are measured by standard procedure available in the literatures.

Theory and Calculation:

Relative density formulae:

R.D. =[Mass of liquid/Mass of water]x ρ_w

Where, ρ_w is density of water

Using the measured data and by using the following formulae,the acoustics parameters have been calculated.

1) Adiabatic Compressibility

$$\beta=\frac{1}{U^2\rho}$$

2) Acoustic Impedance

$$Z = U \times \rho$$

3) Intermolecular free length (Lf) has been calculated from relation.

$$L_f=K_T\sqrt{\beta}$$

Where K_T is a temperature depended constant (Jacobson constant)

T- Absolute temp,

$$K= (93.875 + 0.375 \times T) \times 10^{-8}$$

Results and Discussion

The acoustical parametersare calculated for various system of methyl acetate(MA), ethyl acetate(EA), n-butyl acetate (BA) with 1, 4- Dioxane and water ternary mixtures from the ultrasonic velocities. The experimentally determined values of density (ρ), ultrasonic velocity,(U) adiabatic compressibility (β), acoustic impedance(Z) and free length(L_f)for all the three liquid systems at 296.15 K are given in table (1 to 3). This data are discussed in the light of molecular interaction between the components.

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System-I

Table No 1: - Acoustic parameter for MA + 1, 4 Dioxane + water mixture

Mole fraction		Density ρ= kg/m^3	Ultrasonic velocity U = m/s	Adiabatic compressibility β x 10^{-7} $kg^{-1}ms^2$	Acoustic impedance z = $kgm^{-2}s^{-1}$	Free length L_f A^0
MA X_1	Dw X_3					
0.0104	0.6478	1.0350	1500	4.29	1552.5	1.32773
0.0216	0.6238	1.0347	1372	5.1342	1419.60	1.46792
0.0337	0.5981	1.0322	1520	4.1932	1568.94	1.32656
0.0468	0.5702	1.0296	1448	4.6322	1490.86	1.39437
0.0610	0.5401	1.0267	1440	4.6971	1478.44	1.40400

System-II

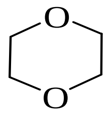
Table No 2: - Acoustic parameter for EA + 1, 4 Dioxane + water mixture

Mole fraction		Density ρ= kg/m^3	Ultrasonic velocity U = m/s	Adiabatic compressibility β x $10^{-7}kg^{-1}ms^2$	Acoustic impedance z = $kgm^{-2}s^{-1}$	Free length L_f A^0
E_A X_1	Dw X_3					
0.0084	0.6490	1.0337	1492	4.3457	1542.20	1.35053
0.0176	0.6264	1.0313	1488	4.3793	1534.57	1.35565
0.0275	0.6019	1.0283	1468	4.5126	1509.54	1.37614
0.0383	0.5753	1.0273	1444	4.6684	1483.42	1.39970
0.0501	0.5463	1.0232	1440	4.7131	1473.40	1.40646

System-III

Table No 3:- Acoustic parameter for B A + 1, 4 Dioxane + water mixture

Mole fraction BA X_1	Mole fraction Dw X_3	Density ρ= kg/m^3	Ultrasonic velocity U = m/s	Adiabatic compressibility β x 10^{-7}kg^{-1}ms^2	Acoustic impedance z = kgm^{-2}s^{-1}	Free length L_f A^0
0.0062	0.6505	1.0352	1464	4.507	1515.53	1.37532
0.0131	0.6293	1.0322	1488	4.375	1535.91	1.35504
0.0205	0.6062	1.0267	1476	4.470	1515.40	1.36958
0.0286	0.5811	1.0224	1432	4.769	1464.07	1.41466
0.0375	0.5554	1.0193	1436	4.757	1463.71	1.41302



1, 4 Dioxane Molecular formula- $C_4H_8O_2$ Structural formula 1-4 dioxane

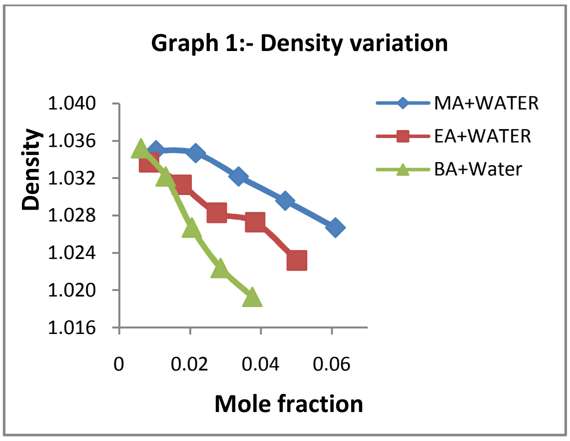
Density (ρ):

In all the three systems, the density decreases with increases in mole fraction of ester, due to the decreasing value of density and ultrasonic velocity show that there is less attraction between solute and solvent molecule. As the number of hydrocarbon group or the chain length of ester increase, a gradual decrease in sound velocity was observed. This behavior at these concentrations is different from behavior of ideal mixtures and can be attributed to intermolecular interaction in the system studied.

The plot of mole fraction against density for the three systems is given in following graph 1.

Ultrasonic velocity (U):

In all the three liquid system it has been investigated that the ultrasonic velocity decreases with increase mole fraction of ester.



Shown in table (1, 3) it is observed that as the number of hydrocarbon group or chain length of ester increases, gradual decrease in sound velocity. This property at such concentration is quite different from ideal mixture. This suggests that there are molecular interactions between the components of other mixtures. The decrease in ultrasonic velocity is due to dissociation in aqueous solution of ester + 1, 4 Dioxane.

The ultrasonic velocity in a mixture depend upon the increase or decrease of intermolecular free length.

Adiabatic compressibility (β):

The adiabatic compressibility is fractional decrease of volume per unit increase of pressure, when there is no loss or gain of heat. These changes are related to compressibility of liquid mixture.

The adiabatic compressibility value for various composition of ternary mixtures have been calculated from the ultrasonic velocities of ester. In present investigation in all the three system it's shown in table (1, 3) noted that adiabatic comparability increases with increase mole fraction of ester. It may be due to increase in chain length of ester, indicating relative stronger hydrogen bonding over wide range of concentration. The increase adiabatic compressibility will separate molecule to distorted packing resulting in to increase of intermolecular free length. The compressibility data also shows that dipole-dipole attraction is stronger in ester, 1, 4 -Dioxane and water ternary mixtures.[Thirumaran, S. et. al. 2010 & Thirumaran S, Sudha, S. et. al. 2010]

Acoustic impedance (Z):

The ratio of instantaneous pressure excerpt at any particle of medium to the instantaneous velocity of that particles known as specific acoustic impedance.

All the three systems are studied and it's observed that the value of acoustic impedance decreases with increase in concentration of ester i.e. MA, EA, n-BA listed in table 1-3. The decrease in acoustic impedance with mole fraction can be explain on the basis of internal lyophobic interaction between solute and solvent molecules1 (Aswale S.S. et.al.2013 & Kannappan A.N. et.al. 2009) which increase intermolecular distance between the molecules. The decreasing trend of acoustic impedance (Z) suggests that decrease in molecular packing in liquid medium. The acoustic impedance contributes to explain molecular interaction.

Linear free length (L_f):

Intermolecular free length is predominating factor in determining the variation of speed of sound in liquid mixture. In present investigation it is noted that in all the three system, intermolecular free length increases with increase in concentration of ester (Table 1, 3). Intermolecular free length is related to ultrasonic velocity. As the ultrasonic velocity decreases due to increases concentration of ester, the intermolecular free length increase and vice –versa [Janna V.et. al. 2008]The increase in concentration leads to decrease in gap between two spaces and which know as intermolecular free length. The change in free length also indicates that there is a significant interaction between solvent and solute molecule due to which structural rearrangement is also affected. The increase of free length indicates structure promoting behavior of solute molecule.

Conclusion

The various acoustical parameter such as adiabatic compressibility, acoustic impendence and free length have been evaluated from ultrasonic velocity and density for ternary liquid mixtures for the system I, II, III at 296.15 K. in the present investigation its inferred that there are intermolecular interaction among the components of ternary liquid mixtures leading to the possible hydrogen bond formation between unlike molecules. Molecular interaction increases with the increase in mole fraction of ester i.e. MA, EA, n-BA, in all the three system.

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