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European Journal of Applied Engineering and Scientific Research, 2014, 3 (3):5-8
(http://scholarsresearchlibrary.com/archive.html)

ISSN: 2278 – 0041
CODEN(USA): EJAEAJ)

Ultrasonic studies on molecular interactions in the binary mixtures of n-butanol with acetone and ethyl methyl ketone

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ABSTRACT

Sound velocity, density and viscosity values have been measured for the binary mixtures of n-butanol with acetone and ethyl methyl ketone at 303K. From the measured data, acoustical parameters such as, adiabatic compressibility (β), intermolecular free length (L_f), internal pressure (π_i) and acoustic impedance (Z) have been estimated using the standard relations. These values have been used to substantiate the existence of intermolecular interaction present in liquid mixtures.

Keywords: Ultrasonic velocity, adiabatic compressibility, free length, Hydrogen bonding.

INTRODUCTION

The ultrasonic velocity technique has been a subject of active interest during recent past to study the nature of molecular interaction in liquid and liquid mixtures [1-3].Properties such as densities, viscosities and ultrasonic velocities and their variation with composition and temperature of the binary mixture are useful to design engineering process and in chemical and biological industries. The study on changes in these properties of mixtures has been found to be an excellent qualitative and quantitative way to bring out the information about molecular structure and intermolecular forces present in the liquid mixtures.

Since the ultrasonic method is a versatile technique for studying the physical properties that provide a lot of information about molecular interactions in various solutions, in the present investigation, we have studied important ultrasonic parameters like adiabatic compressibility (β_{ad}), intermolecular free length (L_f), internal pressure (π_i) and specific acoustic impedance (Z) for the solutions of n-butanol with acetone and ethyl methyl ketone at 303K. The investigations regarding the molecular interactions in binary liquid mixtures having an alcohol as one component is of particular importance since alcohols are strongly self associated liquids with a three dimensional network of hydrogen bonds and can be associated with any other group having some degree of polar interactions[4,5]. Owing to these considerations, an attempt has been made to elucidate the molecular interactions in the mixtures of n-butanol with acetone and ethyl methyl ketone.

MATERIALS AND METHODS

The Chemicals used in the present work were analytical reagent and spectroscopic reagent grades with minimum assay of 99.9% were obtained from E-Merck Ltd. (India) and Sd Fine Chemicals, which are used as such without further purification.

Ultrasonic velocity, density and viscosity measurements on liquid mixtures were made at the temperature of 303K by using F 81 Ultrasonic interferometer (Mittal Enterprises, New Delhi) at a frequency of 2 MHz with an accuracy of ±0.2%, specific gravity bottle of capacity of 10ml with accuracy of ± 0.0001g cm^{-3} and the Ostwald's viscometer accurate to ± 0.1% respectively.

Acoustical Parameters

In the present study, the ultrasonic velocity, density and viscosity measurements were carried out in the binary mixtures of n-butanol with acetone and ethyl methyl ketone at 303K with different concentrations**.** Using the measured values of density (ρ) and ultrasonic velocity (U), the related acoustical parameters [6, 7] were calculated as detailed below.

The adiabatic compressibility (β_{ad}) has been calculated using the relation

$$\beta_{ad} = [U^2\rho]^{-1} \quad \ldots(1)$$

where, ρ is the density of the solution and U is the ultrasonic velocity of the solution.

The intermolecular free length (L_f) has been calculated using the formula

$$L_f = K_T [\beta_{ad}]^{1/2} \quad \ldots(2)$$

where, K_T is a constant for different temperatures known as Jacobson constant [8]

The Specific acoustic Impedance:

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

Internal pressure;

$$\pi_i = bRT [K\eta / U]^{1/2}[\rho^{2/3} / M_{eff}^{7/6}] \quad ...(4)$$

Where b stands for the cubic packing factor which is assumed to be 2 for all liquids and solutions, K, the temperature independent constant ($4.28X10^9$), R, the gas constant (8.3143 J $K^{-1}mol^{-1}$) , T, the absolute temperature and M_{eff} is the effective molecular weight of the solution.

Then these parameters are correlated with concentration of n-butanol.

RESULTS AND DISCUSSION

The experimentally determined values of density (ρ), viscosity(η) and ultrasonic velocity (U) at 303K and the calculated values of adiabatic compressibility (β), intermolecular free length (L_f), and acoustic impedance (Z) and internal pressure (π_i) have been presented in the Table 1 for the System I : n-butanol + acetone and System II : n-butanol + ethyl methyl ketone.

It can be seen from the Table 1 that the ultrasonic velocity increases with increase in mole fraction of alcohol for both the mixtures. This behavior at such concentrations is different from the ideal mixtures behavior, which indicates the presence of molecular association between solute and solvent. The variation of ultrasonic velocity in a solution depends upon the increase or decrease of intermolecular free length after mixing the components, on the basis a model for propagation proposed by Eyring and Kincaid [9]. The increase in velocity may be due to the structural changes of molecules in the mixture take place due to the existence of electrostatic field between the

interacting molecules. Thus the structural arrangement of molecules results in the effect of adiabatic compressibility (β).

In both the systems, the adiabatic compressibility and free length decreases with increase in concentration of butanol. The adiabatic compressibility shows an inverse behavior as compared to ultrasonic velocity. It indicates that there is a significant interaction between solute and solvent molecules. The addition of interacting molecules may break up the molecular clustering of the other, releasing several dipoles for interaction, which suggest that hydrogen bond association. In view of greater forces of interaction between solute and solvent molecules forming hydrogen bonding, there will be a decrease in free length and compressibility. Similar results were also reported in some liquid mixtures [10,11]

It is noticed that as the concentration of alcohol increases, free volume decreases where as the internal pressure increases. Due to this close packing of the molecules inside the shield takes place. The increase in internal pressure generally indicates association through hydrogen bonding and hence it supports the present investigation [12]

Table 1: Experimental values of acoustical parameters of binary mixtures as a function of molar concentration of n-butanol at 303K

Mole fraction X_1	U ms^{-1}	ρ Kgm^{-3}	ηx10^{-3} Nsm^{-2}	β x10^{10} m^2N^{-1}	L_f x10^{11} m	π_i x10^{-8} Nm^{-2}	Z x10^{-3} Nsm^{-3}
System I : n-butanol + acetone							
0.1	1152	794	0.570	9.490	6.146	1.685	914.6
0.2	1167	795	0.830	9.236	6.063	1.960	927.7
0.3	1174	797	1.081	9.103	6.019	2.166	935.6
0.4	1183	799	1.332	8.943	5.966	2.333	945.2
0.5	1197	801	1.592	8.713	5.899	2.426	958.7
0.6	1202	803	1.841	8.619	5.857	2.577	965.2
0.7	1214	805	2.090	8.428	5.792	2.664	977.2
0.8	1223	806	2.341	8.294	5.746	2.737	985.7
0.9	1232	808	2.603	8.153	5.697	2.805	995.4
1.0	1240	810	2.801	8.029	5.653	2.833	1004.4
System II : n-butanol + ethyl methyl ketone							
0.1	1184	798	0.670	8.939	5.965	1.444	944.8
0.2	1190	799	0.910	8.838	5.931	1.674	950.8
0.3	1197	800	1.161	8.724	5.893	1.881	957.6
0.4	1203	802	1.405	8.615	5.856	2.055	964.8
0.5	1209	803	1.646	8.519	5.823	2.216	970.8
0.6	1215	804	1.881	8.425	5.791	2.362	976.8
0.7	1221	806	2.129	8.322	5.755	2.495	984.1
0.8	1228	807	2.374	8.217	5.719	2.627	990.9
0.9	1234	809	2.616	8.117	5.684	2.746	998.3
1.0	1240	810	2.852	8.029	5.653	2.858	1004.4

When an acoustic wave travels in a medium, there was a variation of pressure from particle to particle. The ratio of the instantaneous excess pressure at any particle of the medium to the instantaneous velocity of that particle is named as specific acoustic impedance of the medium. This factor is ruled by the inertial and elastic properties of the medium. It is important to examine specific acoustic impedance in relation to concentration and temperature. When a plane ultrasonic wave is set up in a liquid, the pressure and hence density and refractive index show specific variations with distance from the source along the direction of propagation [13]. In the present inquiry, it was observed that these acoustic impedance (Z) values increases with increasing concentration of n-butanol. Such a continuous increasing values of acoustic impedance (Z) further supports the possibility of molecular interactions between the unlike molecules.

CONCLUSION

In the present investigation, the various acoustical parameters such as adiabatic compressibility, free length, internal pressure and acoustic impedance have been evaluated from ultrasonic velocity, density and viscosity for the binary liquid mixtures of n-butanol with acetone and ethyl methyl ketone at 303K. From the above studies it is concluded

that the interactions are present between the butanol + acetone and ethyl methyl ketone and these interactions are observed to be increasing with increase of mole fraction of n-butanol.

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