International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 9 Issue 7 ǁ 2021 ǁ PP. 66-69

Ultrasonic Study of Molecular Interaction in Binary Liquid Mixture 1- Pentanol and *N-N* dimethylformamide (DMF) at 298 K

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Abstract
The ultrasonic velocity, density and viscosity have been measured for the mixture 1-pentanol with N-N dimethylformamide (DMF) at 298 K. The experimental data have been used to calculate the acoustical parameters namely adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i). The excess values of the above parameters are also evaluated and discussed in the light of molecular interaction existing in the mixture. It is obvious that there is a formation of hydrogen bonding between DMF and 1-Pentanol. Further, the addition of DMF causes dissociation of hydrogen bonded structure of 1-Pentanol. The valuated excess values confirm that the molecular association is more pronounced in mixture.

Keywords: *Adiabatic compressibility, Free length, Free Volume, Hydrogen bonding, Internal pressure.*

Date of Submission: 06-07-2021 Date of acceptance: 20-07-2021

I. INTRODUCTION

Ultrasonic studies provide a wealth of information about the state of liquids. The measurement of ultrasonic velocity in pure liquids and mixtures is an important tool to study the physiochemical properties of the liquids and also explain the nature of molecular interactions. The practical importance of liquid mixture rather than single component liquid systems has gained much importance during the last two decades in assessing the nature of molecular interactions and investigating the physio-chemical behavior of such systems[1-2]. Ultrasonic investigation of liquid mixtures consisting of polar and non-polar components is of considerable importance in understanding the physical nature and strength of molecular interaction in the liquid mixtures[3]. For a better understanding of the physio-chemical properties and the molecular interaction between the participating components of the mixtures, ultrasonic velocity together with density and viscosity are measured for different concentrations of the components in the mixture. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components[4 -6] as well as strongly interacting components[7]. The study of molecular association in organic ternary mixtures having alcohol as one of the components is of particular interest, since alcohols are strongly self-associated liquid having a three dimensional network of hydrogen bond[8] and can be associated with any other group having some degree of polar attractions[9]. Ultrasonic velocity and the derived acoustical parameters like adiabatic compressibility, free length, free volume, internal pressure, etc., provide valuable information about the molecular environments[10].

DMF (C_3H_7NO) is a versatile compound. It is a non-aqueous solvent which has no hydrogen bonding in pure state. Therefore, it acts as an aprotic, photophilic medium with high dielectric constant and it is also considered as a dissociating solvent. DMF being a polar molecule results in dipolar and induced dipolar interaction between it and chlorobenzene in addition to dipolar-dipolar interaction between its molecules. DMF is primarily used as an industrial solvent. DMF solutions are used to process polymer fibers, films and surface coating to permit easy spinning of acrylic fiber to produce wire enamels and as a crystallization medium in the pharmaceutical industry[23].

1-Pentanol is an alcohol with five carbon atoms and the molecular formula $C_5H_{11}OH$. 1-Pentanol is a colourless liquid with a distinctive aroma. It is the straight-chain form of amyl alcohol, one of 8 isomers With that formula. The hydroxyl group is the active site of many reaction. 1-Pentanol can be used as a solvent for coating CDs and DVDs. 1-Pentanol can be prepared by fractional distillation of fusel oil. To reduce the use of fossil fuels, research is underway to develop cost-effective methods of producing (chemically identical) bio-pentanol with fermentation., it is widely used as a solvent because many organic materials are soluble in it.

Since, no effort appears to have been made to collect the ultrasonic velocity data for the binary mixture of 1-Pentanol with DMF at 298K. This experimental study was carried out by the author and reported the present investigation. The present binary liquid system taken up for study at 298K.

II. EXPERIMENTAL

The chemicals used in the present work were analytical reagent (AR) and spectroscopic reagent (SR) grades with minimum assay of 99.9% were obtained from Sd fine chemicals India. The various concentrations of the binary liquid mixture were prepared in terms of mole fraction, such as 1-Pentanol with DMF varied from 0.1 to 0.9. The density of pure liquids and liquid mixture were determined using a specific gravity bottle by relative measurement method with a reproducibility of ±0.01 $kg.m^{-3}$ (Model: SHIMADZU AX-200). An Ostwald's viscometer of 10 mL capacity was used for the viscosity measurement of pure liquids and liquid mixtures and efflux time was determined using a digital chronometer to within ±0.01s. An ultrasonic interferometer (Model: F81) supplied by M/s. Mittal Enterprises, New Delhi, having the frequency 3MHz with an overall accuracy of ±2 ms^{-1} has been used for velocity measurement. An electronically digital constant temperature bath (RAAGA Industries, Chennai) has been used to circulate water through the double walled measuring cell made up of steel containing experimental mixtures at the desired temperature. The accuracy in the temperature measurement is ± 0.1K.

III. THEORY

Using the measured data, the following acoustical parameters have been calculated Adiabatic Compressibility[11]

$$\beta = 1/U^2\rho \qquad \text{..........} (1)$$

Intermolecular free length (L_f) has been calculated from relation[12],

$$Lf = KT\sqrt{\beta} \qquad \text{..........} (2)$$

Where K_T is a temperature dependent constant. Free volume (V_f) has been calculated from relation[13],

$$V_f = (M_{eff}U/K\eta)^{3/2} \qquad \text{..........} (3)$$

Where M_{eff} is the effective molecular weight ($M_{eff} = \Sigma$ mi xi, in which mi and xi are the molecular weight and the mole fraction of the individual constituents respectively). K is a temperature independent constant which is equal to 4.28×10^9 for all liquids.The internal pressure (π_i) can be found out as[14]

$$\pi_i = bRT\,(K\eta/U)^{1/2} \times (\rho^{2/3}/M_{eff}^{7/6}) \qquad \text{..........}(4)$$

K is a constant, T the absolute temperature, η the viscosity in Nsm^{-2}, U the ultrasonic velocity in ms^{-1}, ρ the density in Kgm^{-3}, M_{eff} the effective molecular weight. Excess parameter (A^E) has been calculated by using the relation[15]

$$A^E = A_{exp} - A_{id} \qquad \text{..........} (5)$$

Where, $A_{id} = \sum_{i=0}^{n} Aix_i$, A_i is any acoustical parameters and x_i the mole fraction of the liquid component.

IV. RESULTS AND DISCUSSION

The experimentally determined values of density (ρ), viscosity (η) and ultrasonic velocity (U) of binary liquid mixture at 298 K are represented in Table 1. The values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) of the liquid mixture are evaluated and are presented in Table 2. The respective excess values of above parameters have been also evaluated and presented in Table 3. In the present investigation, in the liquid mixture, except viscosity and all the other parameters such as density and ultrasonic velocity decreases with increasing molar concentrations of alcohols. It is observed that as number of hydrocarbon group or chain length of alcohol increases, a gradual decrease in ultrasonic velocity is noticed. This behaviour at such concentrations is different from the ideal mixture's behaviour can be attributed to intermolecular interactions in the systems studied[16-17]. The value of adiabatic compressibility (β) shows an inverse behaviour as compared to the ultrasonic velocity (U).The adiabatic compressibility (β) increases with increase of concentration of molar concentration of 1-Pentanol. It is primarily the compressibility that increases due to structural changes of molecules in the mixture leading to a decrease in ultrasonic velocity.

Table 1. Density (ρ), viscosity (η) and ultrasonic velocity (U) at 298 K

Mole fraction		Density(ρ)/kg/m^3	Viscosity(η)/10^{-3}Nsm	Ultrasonic velocity(U)m/s
X_1	X_2			
0.1000	4.254	898.58	0.7254	1398.4
0.2995	4.682	847.24	0.8024	1325.2
0.4998	5.854	786.45	0.9458	1298.8
0.7728	7.025	748.31	1.0024	1254.5
0.9000	8.368	721.23	1.1487	1185.6

Table 2. Adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) at 298 K

Mole fraction		Adiabatic compressibility (β)/10^{-10}m^{2}N^{-1}	Free length L_f / 10^{-10}m	Free volume V_f/10^{-7}m^3 mol^{-1}	Internal pressure π_i /10^6 N^{-2}m
X_1	X_2				
0.1000	4.254	4.4587	0.3858	1.6985	298.32
0.2995	4.682	4.9854	0.4258	1.2012	322.45
0.4998	5.854	6.0246	0.4858	1.0089	398.66
0.7728	7.025	6.8758	0.5424	0.6554	452.43
0.9000	8.368	7.0245	0.6588	0.3664	512.02

Table 3. Excess values of adiabatic compressibility (β^E), free length ($L_f{}^E$), free volume ($V_f{}^E$) and internal pressure ($\pi_i{}^E$) at 298 K

Mole fraction		Excess Adiabatic compressibility (β^E)	Excess Free length($L_f{}^E$)	Excess Free volume ($V_f{}^E$)	Excess Internal pressure($\pi_i{}^E$)
X_1	X_2				
0.1000	5.5845	-0.2154	6.0202	0.2585	-32.458
0.2995	5.8578	-0.4252	8.8558	0.9689	-46.258
0.4998	6.2528	-0.4858	9.2365	1.3220	-62.854
0.7728	7.2524	-0.2542	9.0030	2.2522	-68.232
0.9000	8.2525	-0.1202	1.4258	3.0475	-38.587

Such a continuous increase in adiabatic compressibility with respect to the solute concentration has been qualitatively ascribed to the effect of hydrogen bonding or dipole dipole interactions[18]. *N-N* dimethylformamide (DMF) is a non-aqueous solvent of particular interest, because it has no hydrogen bonding in pure state. Therefore, it acts as an aprotic protophilic medium with high dielectric constant and it is considered as a dissociating solvent. Further, the addition of *N*, *N*-Dimethylformamide (DMF) with mixture causes dissociation of hydrogen bonded [19, 23]structure of 1-Pentanol.

Further, mixing of DMF with 1-Pentanol causes dissociation of hydrogen bonded structure of 1-Pentanol and subsequent formation of (new) H-bond (C = O … H –O) between proton acceptor oxygen atom (with lone pair of electrons) of C=O group of DMF and hydrogen atom of –OH group of 1-Pentanol molecules. This dissociation effect leads to an decrease in volume and hence an increase in adiabatic compressibility[20]. Further, the molecules of 1- Pentanol are self-associated in pure state through hydrogen bonding. However mixing of DMF with 1-Pentanol would release the dipoles of 1- Pentanol and interact with DMF molecules forming strong hydrogen bonds, leading to contraction in volume which makes an increase in free length in the liquid mixture. Such an increase in free length may also be attributed due to the loose packing of molecules inside the shield, which may be brought by weakening of molecular interactions[21].

Further, a decrease in free volume (V_f) and an increase in internal pressure (π_i) with increase in concentration of the 1- Pentanol is noticed in the liquid mixture. The increase in internal pressure generally indicates association through hydrogen bonding and hence supports the present investigation. Similar results were observed by earlier workers[22-23] in which an increase in internal pressure generally indicates association through hydrogen bonding. In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in term of excess parameter rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behaviour with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions. The extent of deviation depends upon the nature of the constituents and composition of the mixture[23]. It is learnt that negative excess values is an indication of strong molecular interaction in the liquid mixture, whereas positive excess values attributed to weak interactions, which mainly results from the dispersion forces.

As far as excess values are concerned, in the liquid mixture, excess adiabatic compressibility (β^E) values are negative and however, the excess values of free length ($L_f{}^E$) and free volume ($V_f{}^E$) are all positive. These are represented in the Table 3. Such a positive deviation show that the mixture is behaving as non-ideal ones, on the basis of sound propagation given by Eyring *et.al*[24]. The positive values of free volume indicate that weakening of hydrogen bonding between 1- Pentanol and DMF and also dissociation of 1-Pentanol molecule. The negative excess internal pressure ($\pi_i{}^E$) in the liquid mixture clearly confirms this.

V. CONCLUSION

From ultrasonic velocity, related acoustical parameters and their excess values for the binary liquid mixture of 1-Pentanol with DMF at 298 K, it is concluded that there is a formation of hydrogen bonding between DMF and 1-Pentanol. Further, the addition of DMF causes dissociation of hydrogen bonded structure of 1-Pentanol. The evaluated excess values clearly confirm that that the molecular interaction is more pronounced.

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