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Acoustical and excess thermodynamical parameters of binary liquid mixtures at 308K and 2 MHz frequency

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ABSTRACT: *The density, ultrasonic velocity and viscosity at the temperature 308K and 2MHz frequency have been measured in the binary system of Cinnamaldehyde with the liquid acetone. From the experimental data of the density, ultrasonic velocity and viscosity, various acoustical parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f) and the free volume (V_f) were calculated. These parameters throw the light on the solute-solvent and dipole-dipole interactions. Excess parameters like V_f^E, β_a^E, L_f^E are evaluated for the system investigated. From the properties of these excess parameters, the nature and the strength of interactions in this binary system are discussed. It has been observed that, weak dispersive type intermolecular interactions are confirmed in the systems investigated. The results are interpreted in terms of molecular interaction between the components of the mixtures.*

Keywords: *Acoustical parameters, Acetone, binary liquid mixtures, Cinnamaldehyde, Molecular interactions, and Ultrasonic velocity.*

I. INTRODUCTION

Ultrasonic waves have been used by many scientists to investigate the nature of molecular interactions and physico-chemical behaviors of pure, binary and ternary liquid mixtures [1-3]. Acoustical parameters are useful in understanding the nature and strength of molecular interactions in the liquid mixtures [4]. Molecular interactions and structural behavior of molecular and their mixtures can be identified using ultrasonic studies [5, 6]. Ultrasonic velocity measurements are used to determine the structure and molecular interactions occurring in the solutions. Among various techniques, ultrasonic velocity measurements have been found to be most powerful tool in the investigation of structure and molecular interactions occurring in the liquid mixtures. The measurement of ultrasonic velocity gives valuable information about the physical properties and strength of molecular interactions in the mixtures [7]. The ultrasonic study of liquid and liquid mixtures has been employed in understanding the nature of the molecular interactions in pure components and their mixtures. The deviation from ideally is expressed by many thermodynamic variables, particularly by excess properties. Further these properties have been widely used to study the molecular interaction between the various species in the mixtures. The excess properties are found to be more sensitive towards intermolecular interaction between the component molecules of liquid mixtures. The sign and extent of deviation of excess properties depend on the strength of interaction between unlike molecules [8-10].

In this study, Cinnamaldehyde and acetone (as a solvent) have been used, because of their important uses in various fields, such as flavoring agent in ice cream and chewing gum, in some natural perfumes, as a food adulterant, in agriculture as a pesticide, in medical field, to prevent oral bacterial growth and as a anti-cancer agent etc for Cinnamaldehyde. Similarly the acetone is also important in the research field because, it is used as a solvent for cleaning purpose in the laboratory. It is naturally produced and disposed off in the human body as a result of normal metabolic processes. A reproductive toxicity test of acetone shows that it has low potential to cause reproductive problems. The body naturally increases the level of acetone in pregnant women, nursing mothers and children because their energy requirement leads to higher level of acetone production. The higher level of acetone in the body reduces epileptic attacks in infants and children.

Therefore we thought worthwhile to study the binary system of Cinnamaldehyde with the solvent acetone. In the present investigation, we report the experimental studies of Ultrasonic velocity (U), Density (ρ) ,Viscosity (η) and derived thermodynamic parameters like adiabatic compressibility (β_a), free length (L_f) , free volume (V_f), excess compressibility (β_a^E), excess free length (L_f^E) and excess free volume (V_f^E) at the temperature 308K. These derived thermodynamic parameters are expected to highlight the role of Cinnamaldehyde with the liquid acetone and its influence with concentrations and temperature.

II. EXPERIMENTAL DETAILS

The ultrasonic velocity (U) in liquid mixtures prepared by taking purified AR grade samples, have been measured using an ultrasonic interferometer (Mittal type, Model F-81) working at 2MHz frequency and at

temperature 308K. The accuracy of sound velocity was ±0.1 ms^{-1}. An electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desire temperature. The density of pure liquids and liquid mixtures was determined using pycknometer by relative measurement method with an accuracy of ±0.1Kgm^{-3}. An Ostwald's viscometer was used for the viscosity measurement of pure liquids and liquid mixtures with an accuracy of ±0.0001NSm^{-2}. The temperature around the viscometer and pycknometer was maintained within ±0.1K in an electronically operated constant temperature water bath. All the precautions were taken to minimize the possible experimental error.

III. RESULTS AND DISCUSSION

Using the experimental data of ultrasonic velocity (U), density (ρ) and viscosity (η), various acoustical parameters such as adiabatic compressibility (β_a), free length (L_f) and free volume (V_f) were calculated by the following equations (1-3).

$\beta_a = (U^2 \rho)^{-1}$ ….. (1)

$L_f = K_T \beta a^{1/2}$ ….. (2)

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

Where, K_T is the temperature dependent constant, K is constant equal to $4.28*10^9$ in MKS system, $M_{eff} = \Sigma x_i m_i$, where x_i is the mole fraction and m_i is the molecular weight of the component.

The excess parameters like excess compressibility (β_a^E), excess free length (L_f^E) and excess free volume (V_f^E) have been calculated using the following standard relation: $A^E = A_{exp} - A_{id}$.

Where, $A_{id} = \Sigma A_i X_i$, where, Ai is any acoustical parameter and Xi is the mole fraction of liquid component.

The measured parameters *viz*., ultrasonic velocity (U), density (ρ), viscosity (η) and calculated parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f) , free volume (V_f), excess compressibility (β_a^E), excess free length (L_f^E) and excess free volume (V_f^E) for the system: Cinnamaldehyde + Acetone at temperature 308K and 2MHz frequency are given in Table-1.

Table-1 shows that, velocity increases with concentration of Cinnamaldehyde in acetone. This indicates that strong intermolecular interaction is observed in the system. The density values also have the same trend with velocity in the system. Viscosity decreases in system, suggesting thereby more association between solute and solvent molecules. From the Table-1 it is observed that, the adiabatic compressibility and free length decreases with increase of mole fraction of the solute in system. This may lead to the presence of specific molecular interaction between the molecules of the liquid mixture. Decrease in intermolecular free length in system leads to positive deviation in sound velocity and negative deviation in compressibility. This indicates that the molecules are nearer in the system. Free volume increases with increasing mole fraction of the solute in system. The observed increase values of V_f are due to close association between solute and solvent. Thus, a progressive increase in free volume in Cinnamaldehyde + Acetone binary mixtures clearly indicates the existence of molecular interaction, due to which the structural arrangement is considerably affected [11-13]. For the systems where dispersion, induction and dipolar forces which are operated by the values of excess viscosity are found to be negative, whereas the positive values shows the existence of specific interactions leading to the formation of complexes in liquid mixtures. This behavior shows that the existence of molecular interaction between the components of mixture for the systems studied.

Fig.-1 and fig.-2 shows that, excess compressibility (β_a^E) and excess intermolecular free length (L_f^E) are positive over the entire mole fraction range. The positive value of 'β_a^E' and 'L_f^E' may be attributed to the dominance of specific interaction arising from the making of hydrogen bonds between hydrogen atom of Cinnamaldehyde and carbonyl oxygen atoms of acetone. The variation of excess compressibility and excess free length (Fig.-1&Fig.-2) are found to be positive in the system studied. The values of βa^E & L_f^E increases with increasing the mole fraction of Cinnamaldehyde. The positive value of βa^E & L_f^E may be attributed to specific interactions like hydrogen bonding and charge transfer. In the present investigation the increasing positive βa^E and L_f^E values shows the strong interaction between the unlike molecules and vice-versa. However from fig.-3, excess free volume (V_f^E), for the system is negative, due to the dominance of dispersion forces. Such existence was confirmed by R.Uvarani et.al [14].

IV. FIGURES AND TABLES

TABLE-1: The experimentally measured values of Velocity (U), Density (ρ), Viscosity (η) , the calculated values of Adiabatic compressibility (β_a), Intermolecular free length (L_f), free Volume (V_f), excess compressibility (β_a^E), excess free length (L_f^E) and excess free volume (V_f^E)for Cinnamaldehyde in Acetone at 308K and 2MHz frequency.

Mole fraction of Cinnamaldehyde in Acetone	ρ (kg/m^3)	U (m/s)	$\eta*10^{-3}$ (CP)	β_a*10^{-10} (Pa^{-1})	L_f*10^{-10} (m)	V_f*10^{-7} (m^3mol^{-1})	β_a^E (Pa^{-1})	L_f^E (m)	V_f^E (m^3/mol)
T=308K									
0.0	775.14	1121.00	0.3536	10.29	0.6595	1.993	0.000	0.000	0.000
0.1	781.43	1118.80	0.3178	10.20	0.6581	2.658	0.449	0.017	-2.007
0.2	786.35	1142.66	0.3044	9.740	0.6424	3.302	0.457	0.019	-4.037
0.3	796.52	1176.66	0.2721	9.068	0.6198	4.565	0.277	0.015	-5.447
0.4	806.88	1202.66	0.2323	8.569	0.6025	6.634	0.270	0.016	-6.052
0.5	814.18	1245.00	0.2106	7.924	0.5794	8.919	0.117	0.012	-6.439
0.6	829.42	1279.33	0.1879	7.366	0.5587	12.08	0.052	0.009	-5.954
0.7	864.57	1304.00	0.1714	6.802	0.5368	15.55	-0.019	0.006	-5.159
0.8	889.42	1329.00	0.1581	6.366	0.5193	19.58	0.035	0.007	-3.793
0.9	961.22	1358.66	0.1468	5.636	0.4886	24.44	-0.202	-0.006	-1.611
1.0	978.00	1383.00	0.1409	5.346	0.4759	28.72	0.000	0.000	0.000

FIG. 1-3: The variations of excess adiabatic compressibility (β_a^E), excess free length (L_f^E) and excess free Volume (V_f^E) w. r. to mole fraction (x) of the system: Cinnamaldehyde + acetone at 308K are shown in Fig.: 1, 2 and 3, respectively.

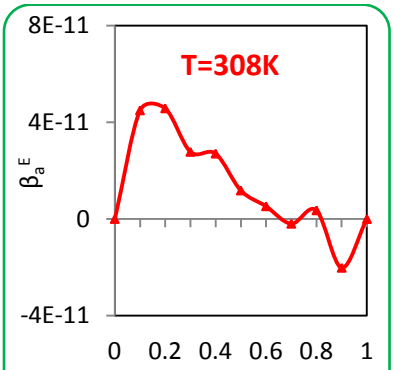

Fig. 1: Mole Fraction of Cinnameldehyde in…

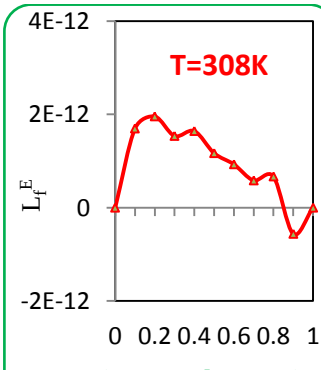

Fig. 2: Mole Fraction of Cinnameldehyde…

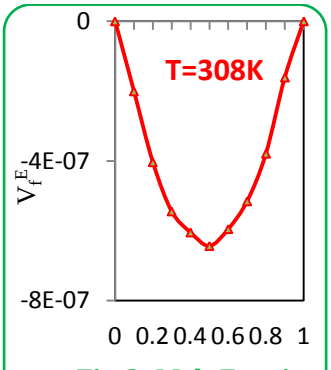

Fig. 3: Mole Fraction of…

V. CONCLUSION

The variation in ultrasonic velocity (U), density (ρ), viscosity (η) and other related thermodynamic parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f), free Volume (V_f), excess compressibility (β_a^E), excess free length (L_f^E) and excess free volume (V_f^E) at various concentrations and at the temperature 308K in the binary solution of Cinnamaldehyde with Acetone shows the variation to be non-linear. Consequently ultrasonic velocity of system increases depending on concentration of Cinnamaldehyde. The observed increase of ultrasonic velocity indicates the solute-solvent interaction. The non linear behavior confirms the presence of solute-solvent, solvent-solvent, and dipole-dipole interactions. For the observed molecular interaction, hydrogen bond formations are responsible for the heteromolecular interaction in the liquid mixture studied. This provides useful information about inter and intra molecular interactions of the mixture as existing in the liquid system. Excess transport properties of binary liquid mixtures of

Cinnamaldehyde in acetone and at 308K are considered to be a reflecting agent of magnitude of polarity and size of the molecules in the interaction. The results of excess properties reveal that the strong molecular interaction exists in the mixtures which may be due to the dominance of hydrogen bonding and charge transfer between the mixing components. The strength of interaction tends to weaker which may due to the presence of weak inter molecular forces and thermal dispersion forces.

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