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THERMODYNAMIC AND ULTRASONIC STUDIES ON BINARY MIXTURES OF ETHYL ACETATE +1-PROPANOL/1-BUTANOL AT 303K.

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Abstract: Various acoustical parameters such as adiabatic compressibility(β), free length(L_f), free volume(V_f), internal pressure(π_i), excess adiabatic compressibility (β^E), excess free length(L_f^E), excess free volume(V_f^E) and excess internal pressure(π_i^E) have been evaluated from density(ρ), viscosity(ŋ) and speeds of sound(U) measurement in two binary liquid mixtures of ethyl acetate with 1-proponal and ethyl acetate with 1-butanol at 303K.These parameters are found to be more sensitive towards the nature and the extent of intermolecular interactions in the binary liquid mixtures.

Keywords: ultrasonic velocity, acoustic Parameters, molecular interaction, excess values.

1. Introduction:

The ultrasonic and thermodynamic studies of liquid and liquid mixtures play an important role in the development of molecular science. Ultrasonic, volumetric and viscometric study of liquid mixture is of substantial importance to understand the physicochemical behaviour of a liquid mixture (Kirandeep kaur and Juglan, 2016). An exhaustive survey of the literature reveals that a substantial amount of work has been done on binary liquid mixtures over a wide range of temperatures (Zahid and Hahn, 2015, Wan Chengran Zhang et al., 2021, Sangeetha Sager et al., 2017). In recent years, the ultrasonic technique has been a more powerful tool in providing information regarding the behaviour of liquids and solids owing to its ability to characterize the physicochemical behaviour of binary and ternary mixtures (Vandana Giratkar et al., 2016).

The ultrasonic and thermodynamic studies of liquid and liquid mixtures are fascinating and of high fundamental practical importance in industry and are used extensively in manufacturing, process control, chemical processing and many other significant fields. The ultrasonic velocity measurements are highly sensitive to molecular interaction and have been particularly informative in elucidating solute–solute/solvent interactions prevailing in the mixtures through the physical nature and strength of the molecular interactions in the liquid mixtures (Soujanya kaki, 2019). The thermodynamic properties in any binary mixtures depict substantial weight on the physical and chemical properties. These properties provide better information necessary for understanding the non-ideal behaviour of complex systems, which are caused by molecular interaction, dipole-dipole interaction etc., of different molecules (Sangeetha Sager et al., 2017)

The study of molecular association on organic ternary mixtures having alcohol as one of the components is of particular interest, since alcohols are strongly self-associated liquids having a three-dimensional network of hydrogen bonds and can be associated with any other group having some degree of polar attraction (Sumathi and Rathnavathi, 2020). Although several investigations were carried out in liquid mixtures having alcohol as one of the components, a systematic study in a series of primary alcohols with ethyl acetate in binary systems has been scarcely reported. This consideration led the author to undertake the present work with the measurement of ultrasonic velocity and evaluation of related acoustical parameters in the binary systems of ethyl acetate +1 propanol and ethyl acetate +1 butanol at 303K.

2. Materials and methods:

All the chemicals used were of Analytical reagent (AR) and Spectroscopic reagent (SR) grades with a minimum assay of 99.9%. The speeds of sound waves were obtained by using an ultrasonic interferometer (Model No, F-81, M/S. Mittal Enterprises, New Delhi) at a fixed frequency of 3 MHz with an accuracy of ± 2 ms^{-1}. An electronically digitally operated constant temperature bath (RAAGA Industries, Madras 61) has been used to circulate water through the double-walled measuring cell made up of steel containing the experimental solution at the desired temperature. The density of pure liquids and liquid mixtures was determined using a pycnometer by relative measurement method with an accuracy of ± 0.1 K (Model: SHIMADZU AX-200). The pycnometer was calibrated at 303.15K with double distilled water and gave an estimated reproducibility of ± 0.0001 gcm^{-3}. An Ostwald's viscometer was calibrated with fresh conductivity water immersed in the water bath which was kept at the

experimental temperature. The time of flow (t_w) of water and the time flow (t_s) of the solution was measured with a digital stop clock having an accuracy ±3 x10^{-6} Nsm^{-2}. The temperature around the viscometer was maintained within ± 0.1 K in an electronically controlled thermostatic water bath. The various concentrations of the binary liquid mixtures were prepared in terms of mole fraction such as 1-pentanol with ethyl acetate and 1-butanol with ethyl acetate varied from 0.1 to 0.7.

2.1 Theory

From the measured values of density (ρ) and ultrasonic velocity (U), viscosity (η), acoustic parameters like adiabatic compressibility (β), intermolecular free length (L_f),free volume (V_f) and internal pressure (π_i) were calculated using the following relations (Sumathi, 2015):

$$\beta = 1/U^2 \rho \quad \ldots (1)$$

$$L_f = K_T \beta^{1/2} \quad \ldots (2)$$

$$V_f = M_{eff} U/\eta K \quad \ldots (3)$$

$$\pi i = bRT (K\eta/U)^{1/2} (\rho^{2/3}/M_{eff}^{7/6}) \quad \ldots (4)$$

Where K_T is the temperature-dependent constant, M_{eff} is the effective molecular weight of the solution, K is the temperature-independent constant (K=4.28 x 10^9), b a constant which is 2 for cubic packing, R the gas constant and T is the temperature in K. The excess parameters (A^E) of all the acoustic parameters were computed by the relation:

$$A^E = A_{exp} - A_{id} \quad \ldots (5)$$

Where $A_{id} = \sum_{i=1}^{n} A_i X_i$, A_i is any acoustical parameter and X_i the mole fraction of the liquid component i.

3. Results and Discussion:

The experimentally determined values of density (ρ), viscosity (η) and ultrasonic velocity (U) of two systems i.e., ethyl acetate +1 propanol and ethyl acetate +1 butanol at 303K are represented in Table 1. The values of adiabatic compressibility (β), free lengthy (L_f), free volume (V_f) and internal pressure (π_i) of the above two systems are evaluated and presented in Table 2. The respective excess values of the above parameters are presented in Figs (1-4).

TABLE-1

Values of Density (ρ), Viscosity (η) and Velocity (U) of systems I & II

Mole Fraction		ρ/(Kgm^{-3})	η/(×$10^{-3}Nsm^{-2}$)	U/(ms^{-1})
X1	X3			
System I: Ethyl acetate + 1-propanol				
0.1000	0.9000	805.17	1.1001	1189.4
0.2000	0.8000	820.35	0.9149	1175.0
0.3000	0.7000	827.41	0.7108	1169.0
0.4000	0.6000	840.18	0.6663	1157.0
0.5000	0.5000	847.90	0.5549	1150.0
0.6000	0.4000	853.47	0.4887	1145.0
0.7000	0.3000	876.12	0.4407	1130.0
System II Ethyl acetate + 1-butanaol				
0.1000	0.9000	823.23	1.453	1205.0
0.2000	0.8000	829.03	1.145	1195.0
0.3000	0.7000	836.61	0.927	1186.0
0.4000	0.6000	843.33	0.777	1176.0
0.5000	0.5000	848.90	0.641	1167.0
0.6000	0.4000	853.33	0.628	1157.0
0.7000	0.3000	870.14	0.524	1145.0

In the present investigation in all the two liquid systems, the values of density increases with increasing mole fraction of ethyl acetate, while the values of viscosity and velocity decreases with increasing the concentration of ethyl acetate. The decrease in ultrasonic velocity with increase in mole fraction of the ethyl acetate is an indication of the existence of interaction between the components of the liquid mixtures (Arul and Palaniapan, 2005). It is observed that as the number of hydrocarbon group or chain length of alcohol increases a gradual decrease in ultrasonic velocity is noted.

The values of adiabatic compressibility (β)(Table 2) show an inverse behaviour as compared to the ultrasonic velocity (U). The deviation in adiabatic compressibility can be explained by taking into consideration of the following factors:

(i) Loss of dipolar association and difference in size and shape of the component molecules lead to a decrease in velocity and an increase in adiabatic compressibility (Rama Rao et al., 2004).

(ii) Dipole–dipole interaction or hydrogen-bonded complex formation between molecules leads to an increase in compressibility. The actual deviation depends on the resultant effect.

The adiabatic compressibility increases while the velocity decreases with an increase in the concentration of ethyl acetate. The increase in compressibility and decrease in velocity is due to the loss of dipolar association and the difference in size and shape of the component molecules present in the system. Similar results were observed by Kumara sastry et al., (Kumara sastry et al., 2012).

TABLE- 2

Values of Adiabatic compressibility (β), Free length (L_f) Internal pressure (π_i) and Free volume (V_f) of Systems I & II

Mole Fraction		$\beta/(\times10^{-10}pa^{-1})$	$L_f/(\times10^{-10}$ m)	$\Pi_i/(\times10^{6}$ pa)	$V_f/(\times10^{-7}$ m^3 mol^{-1})
X1	X3				
System I: Ethyl acetate + 1-propanol					
0.1000	0.9000	8.7851	5.9140	693.019	0.674
0.2000	0.8000	8.8330	5.9301	611.642	0.965
0.3000	0.7000	8.8484	5.9352	517.731	1.456
0.4000	0.6000	8.8912	5.9496	485.936	1.986
0.5000	0.5000	8.9178	5.9585	427.853	2.754
0.6000	0.4000	8.9371	5.9649	387.037	3.148
0.7000	0.3000	8.9400	5.9654	361.664	3.754
System II : Ethyl acetate + 1-butanol					
0.1000	0.9000	8.3680	5.7710	649.970	0.5619
0.2000	0.8000	8.4468	5.7790	567.553	0.8171
0.3000	0.7000	8.4978	5.8165	505.363	1.1369
0.4000	0.6000	8.5740	5.8425	456.574	1.5121
0.5000	0.5000	8.5649	5.8626	412.439	2.0074
0.6000	0.4000	8.6497	5.8934	403.529	2.1077
0.7000	0.3000	8.7235	5.9080	358.326	2.8089

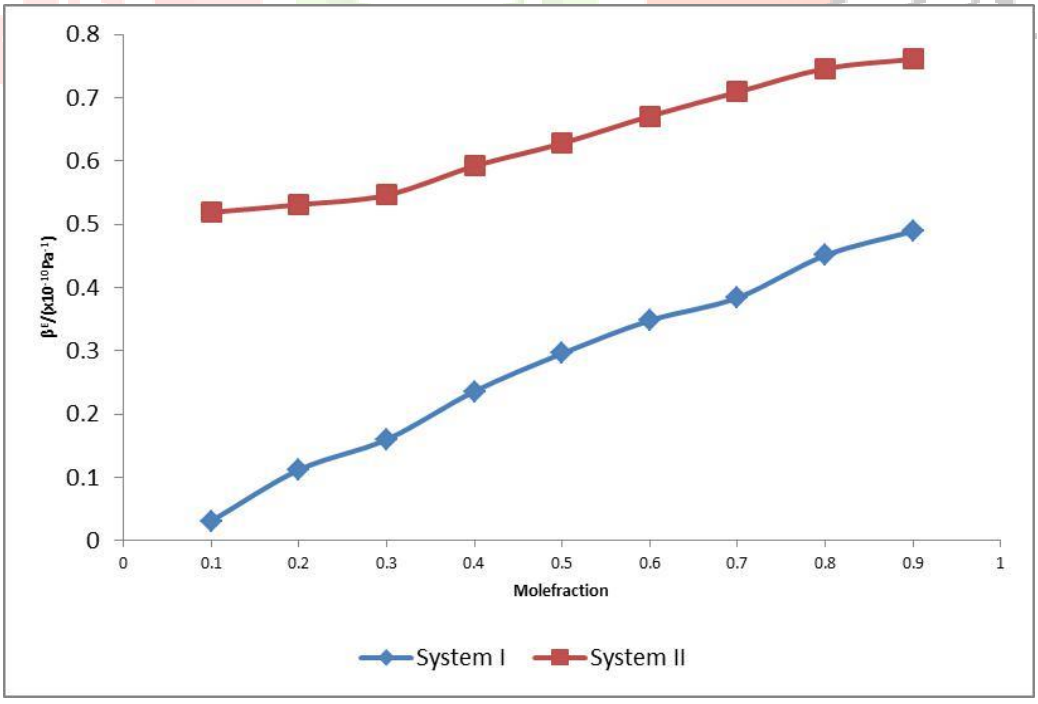

Fig.1: Excess values of Adiabatic compressibility Vs mole fraction of 1-ols

Further, the free length (L_f) (Table 2) increases with an increase in the mole fraction of ethyl acetate. Intermolecular free length is found to be a predominating factor, which depends upon adiabatic compressibility and shows a similar behaviour as that of compressibility. Based on a model for the propagation of sound proposed by Eyring and Kincaid (Eyring and Kincaid, 1938), ultrasonic velocity should decrease if the intermolecular free length increase and vice-versa. This is why the expected increase in free length following the decrease in velocity in nature. The increase in L_f is due to the dominating effect of mutual dissociation of the component molecules in the mixture, which is not compensated by the hydrogen bonding between unlike molecules (Anwar Ali and Anil Kumar Nain, 2000). The β and L_f values increases with the increase in mole fraction of ethyl acetate suggesting the breaking of H-bonding associates present in 1-alkanol molecules resulting in the formation of weak interaction between unlike molecules leading to an increase in β and L_f values.

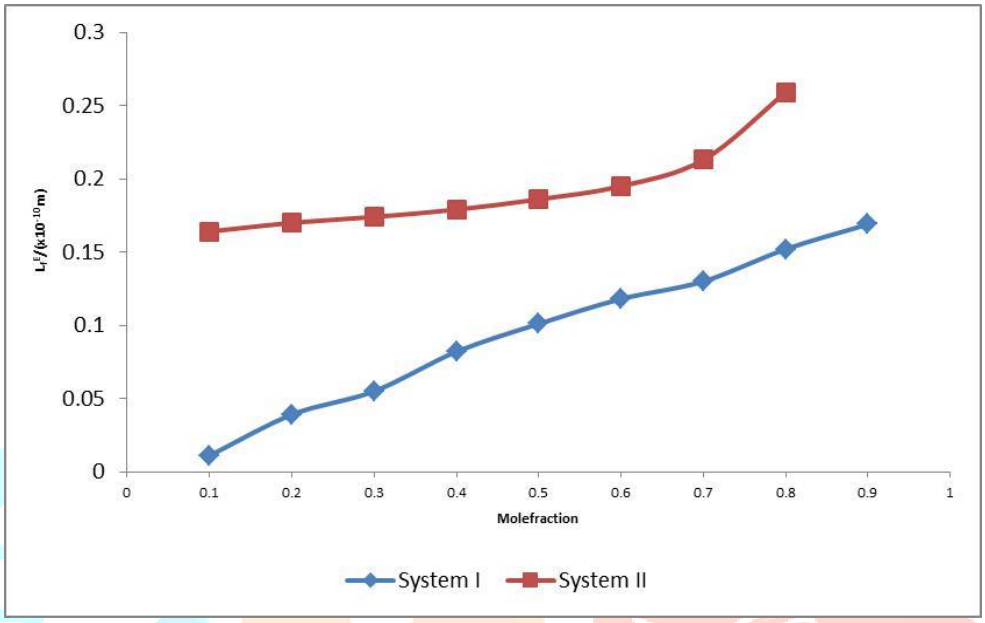

Fig.2: Excess values of Free length Vs mole fraction of 1-ols

Also, the free volume (L_f) (Table 2) increases while the internal pressure (π_i) decreases with an increase in the mole fraction of ethyl acetate. The decrease in π_i with an increase in ethyl acetate concentration indicates the decrease in cohesive forces, which is due to the strength of interaction decreasing, which represents the weak interaction between the molecules (Palani and Meenakshi, 2007).

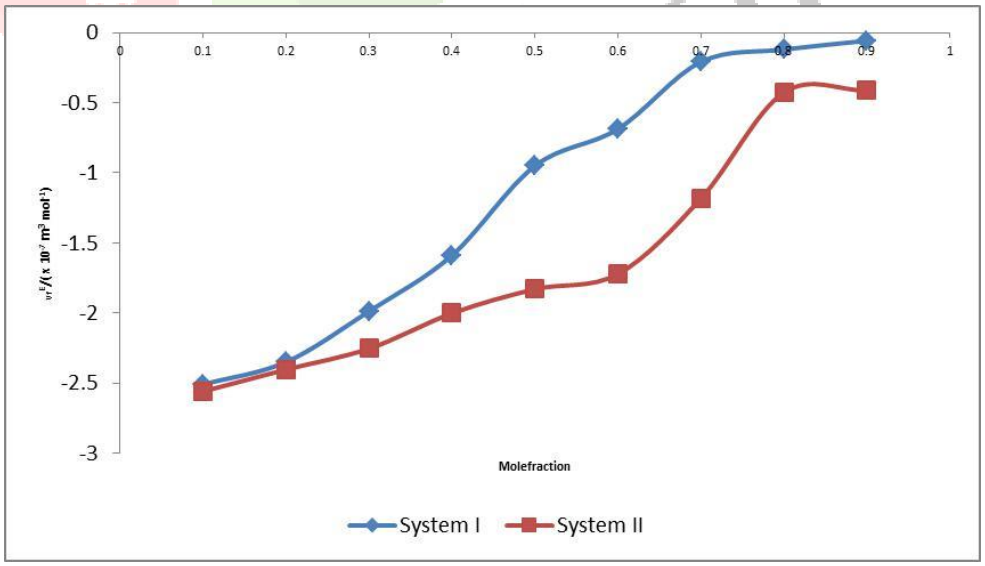

Fig.3 : Excess values of Free volume Vs mole fraction of 1-ols

To understand the nature of molecular interaction between the molecules, it is essential to study the excess parameters. The deviation of the physical property of the liquid mixture from the ideal behaviour is the measure of interaction between the molecules, which is attributed to either adhesive or cohesive forces. The extent of deviation depends upon the nature of the constituents and composition of the mixture. It is learnt that negative excess values are an indication of strong molecular

interaction in the liquid mixture whereas positive excess values are attributed to weak interaction, which mainly results from dispersion forces

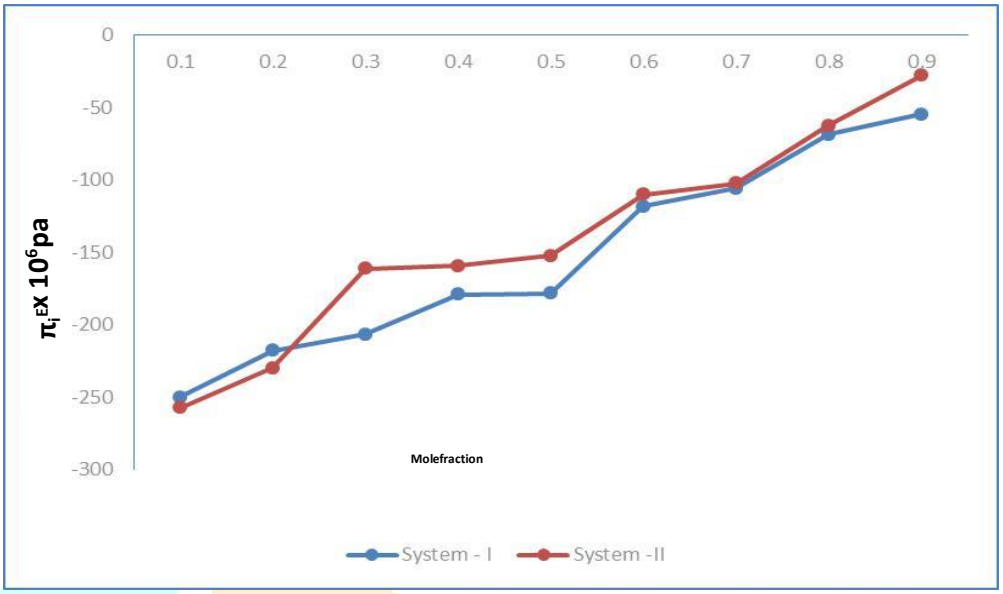

Fig.4:Excess values of Internal pressure Vs mole fraction of 1-ols

In terms of excess parameters, the values of excess adiabatic compressibility (β^E) and excess free length (L_F^E) are positive. The values of β^E and L_F^E depend upon physical and /or chemical contributions. The physical contribution consists of dispersion forces or weak dipole–dipole interaction that leads to positive values of β^E and L_F^E and are mainly due to the weak interaction between the component molecules in the mixture (Sumathi, 2015). Further, the excess free volume (V_F^E) and excess internal pressure (π_i^E) [Figs 3-4] are negative over the entire range of mole fraction in both systems. Fort and Moore (1965) noticed that the negative excess values of these functions indicate a decrease in the strength of interaction between the unlike molecules (Prasad, 2003). The observed negative values of π_i^E confirm only weak molecular interactions are present in our systems studied.

4. Conclusion:

The trends and variation of the present investigation suggest the presence of weak dipolar interaction and dispersion forces between the unlike molecules in all the systems studied. Also, the strength of associative interaction between the unlike molecules weakens with an increase in chain length of alcohols and the order of the interaction is as follows: 1-proponal > 1 butanol i.e the interaction decreases with increases in alkyl chain length of 1-alkanol molecules, probably due to less proton donating tendency of higher alcohols.

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