



Research Journal of Pharmaceutical, Biological and Chemical Sciences

Molecular Interaction studies in Ternary Mixture of Ethyl hydroxy benzoate by Ultrasonic Velocity Measurements

SV Kumara Sastry, Shaik Babu, HA Sie Tiong¹ and S Sreehari Sastry*

*Department of Physics, Acharya Nagarjuna University, Nagarjunangar- 522 510. India.

¹Department of Chemical Science, Faculty of Science, University Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia.

ABSTRACT

The ultrasonic velocity, density and viscosity have been measured for the ternary mixtures of ethyl hydroxy benzoate+ 2-propnol with benzene at 303K. Various acoustical parameters such as adiabatic compressibility (β), inter molecular free length (L_f), free volume (V_f), and acoustical impedance (Z), molar volume (V), Internal pressure (π), Gibb's energy (ΔG^*) and Helmholtz's energy (ΔH^*) are calculated from the values of ultrasonic velocity, density and viscosity that are experimentally measured at 303 K in the ternary system. The Ultrasonic Velocity was measured using a single crystal variable path interferometer working at 2MHz by standard procedure. The densities were measured using a specific gravity bottle by standard procedure and the viscosity was measured using Oswald's viscometer with an accuracy of $\pm 0.1\%$. The results are interpreted in terms of molecular interaction between the components of the mixtures.

Keywords: Ternary Mixture, Ultrasonic velocity, Density, Viscosity, Acoustical parameters, Molecular interaction.

***Corresponding author**

Email: sreehari_ssastry@yahoo.com

INTRODUCTION

Ultrasonic measurements are very useful in chemical and food processing, material testing, under water range cleaning. Ultrasonic's also has wide range of applications in the fields of physics, chemistry, biology and medicine. In recent years ultrasonic investigation find extensive applications in probing in to the physicochemical behavior of binary liquid mixtures leading to an understanding of the liquid state [1-3]. Ultrasonic technique has been adequately employed to investigate the properties of any substance to understand the nature of molecular interactions in pure liquid1 liquid mixtures [2-5] and ionic interactions in electrolytic solutions [6, 7]. Though the molecular interactions studies can be best carried out through spectroscopic methods [8, 9] the other non spectroscopic techniques such as dielectric [10], magnetic [11], ultrasonic velocity and viscosity [12] measurements have been widely used in field of interactions and structural aspect evaluations studies. The measurements of ultrasonic velocity have been adequately employed in understanding the nature of molecular systems and physicochemical behavior in liquid mixtures [13-16].

MATERIALS AND METHODS

EXPERIMENTAL

Chemicals

The chemicals used in the present study are of AR grade (99% of purity) and hence used without further purification.

Measurements

The Ultrasonic Velocity was measured using a single crystal variable path interferometer working at 2MHz by standard procedure. The accuracy of ultrasonic velocity determination in the solution is $\pm 0.001\%$. The velocities were measured at room temperature 303 K. The densities were measured using a specific gravity bottle by standard procedure and the viscosity was measured using Oswald's viscometer with an accuracy of $\pm 0.1\%$.

RESULTS AND DISCUSSION

The calculated parameters such as acoustic impedance (Z), adiabatic compressibility (β), inter molecular free length (L_f), relaxation time (τ), molar volume (V), internal pressure (π_i) and free volume (V_f) are calculated using the following relation (1- 7).

$$Z = \rho U \quad (1)$$

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

$$L_f = K_T \beta^{1/2} \quad (3)$$

$$\tau = \frac{4\eta}{3\rho U^2} \quad (4)$$

$$V = \frac{M_{eff}}{\rho} \quad (5)$$

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

$$V_f = \left[\frac{UM_{eff}}{\eta K} \right]^{3/2} \quad (7)$$

Table 1. Measured Ultrasonic velocity (U), density (ρ) and viscosity (η) and calculated acoustical impedance (Z), adiabatic compressibility (β), free length (L_f), relaxation time (τ) and for Ethyl hydroxybenzoate+2-Propanol with benzene at 303 K.

X_2	U ms ⁻¹	η mPa-s	ρ x10 ³ kg.m ⁻³	Z x10 ³	β x10 ⁻¹⁰ m ² N ⁻¹	L_f x 10 ⁻¹¹ m	τ x 10 ⁻¹³ sec	V x 10 ⁻⁶ m ³ -mol ⁻¹
0.02% of EHB								
90%	1249.6	0.6970	0.8528	1065.7	7.5095	5.4371	6.9788	90.7244
80%	1238.8	0.7276	0.8517	1055.1	7.6509	5.4881	7.4224	82.9161
70%	1217.4	0.7794	0.8480	1032.4	7.9568	5.5967	8.2687	75.3177
60%	1205.0	0.8116	0.8368	1008.3	8.2301	5.6920	8.9060	68.2591
0.03% of EHB								
90%	1244.0	0.7276	0.8619	1072.2	7.4973	5.4327E	7.2736	89.7666
80%	1235.0	0.7595	0.8554	1056.4	7.6651	5.4932	7.7630	82.5613
70%	1214.4	0.7931	0.8520	1034.7	7.9586	5.5973	8.4161	74.9641
60%	1200.0	0.8337	0.8405	1008.6	8.2625	5.7032	9.1848	67.9602
0.04% of EHB								
90%	1250.2	0.7430	0.8619	1077.5	7.4231	5.4057	7.3538	89.6666
80%	1239.4	0.7778	0.8570	1062.2	7.5962	5.4684	7.8786	82.4033
70%	1228.2	0.8070	0.8517	1046.0	7.7839	5.5356	8.3754	74.9940
60%	1208.0	0.8262	0.8464	1022.5	8.0961	5.6455	8.9189	67.4825
0.05% of EHB								
90%	1255.2	0.7556	0.8642	1084.7	7.3445	5.3770	7.3993	89.5277
80%	1239.1	0.7856	0.8591	1064.5	7.5813	5.4631	7.9413	82.2018
70%	1225.4	0.8048	0.8539	1046.4	7.7990	5.5409	8.3692	74.7973
60%	1206.8	0.8280	0.8480	1023.4	8.0971	5.6458	8.9395	67.3568

The measured values such as ultrasonic velocity (U), density (ρ) and viscosity (η) of Ethyl hydroxybenzoate+2-Propanol with benzene are given in Table 1. It is clearly evident that measured parameters like sound velocity, density are decreasing where as viscosity follows increasing trend for decreasing concentration of X_2 . The ultrasonic velocity studies carried out in the present investigation reveal that the velocity varies with concentration due to the solute – solvent interactions through molecular association. The existing particle-particle resistance initiates some more interactions and this is supported by the measured parameters. A keen look at the Table 1 suggest that the range of density, sound velocity, and their variation with concentration of EHB+2Propanol is appreciable, this liquid composition suggests the basis of structural changes as well as interaction between like molecules and unlike molecules. On

comparing the concentrations of EHB+2Propanol with benzene it is evident that the ultrasonic velocity and density keep on decreasing. The shear viscosity increases with increase of concentration once again confirmed the existence of solute – solvent interaction.

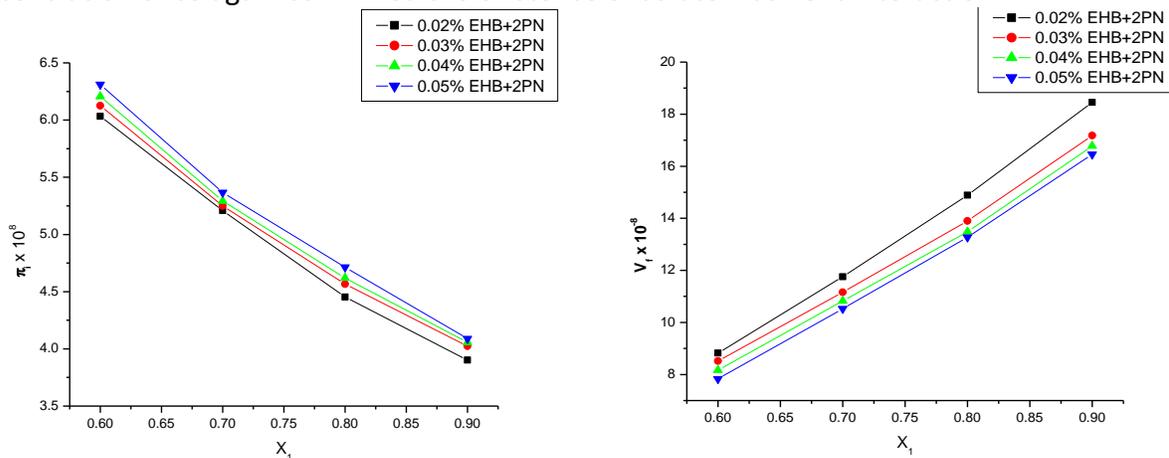


Fig.1 Variation of Internal pressure (π_i) and Free volume (V_f) with X_2 .

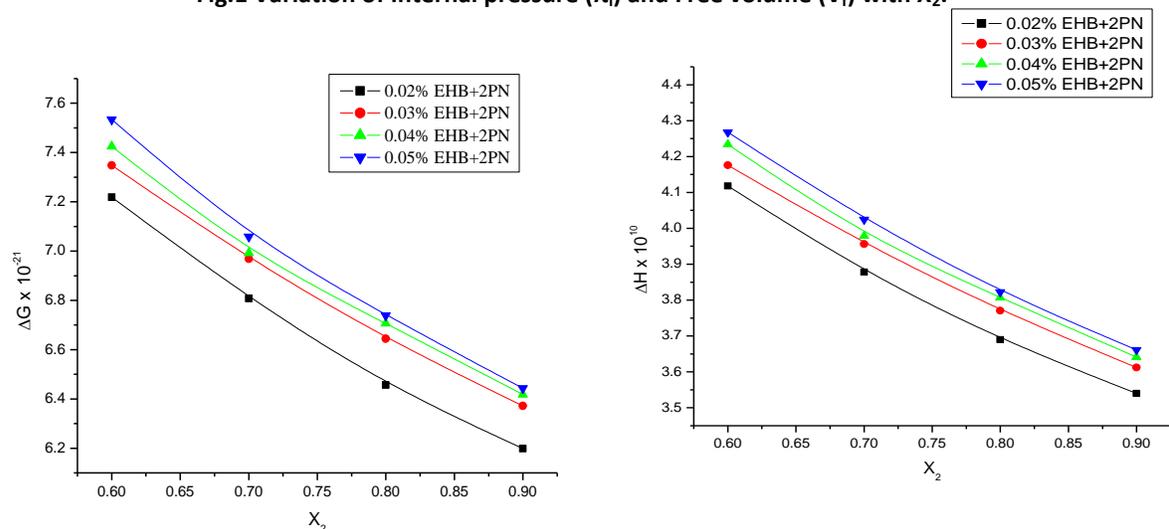


Fig.2 Variation of Gibbs free energy (ΔG) and Helmholtz free energy (ΔH) with X_2 .

The specific acoustic impedance Z is varied linearly with concentration of solution. Adiabatic compressibility (β) shows an increasing trend. The intermolecular free lengths L_f has been calculated by using semi empirical relation given by Jacobson [17]. The values of L_f reflect the same trend as that of β . According to Eyring and Kincaid [18], the ultrasonic velocity increases, if the L_f decreases and vice – a – versa in a result of mixing components. The decrease or increase in the values of L_f can be explained on the basis of interactions between the solute and solvent molecules. Relaxation time shows an increasing trend and molar volume shows a decreasing trend. The computed other parameters like free volume and internal pressure are given in Fig 1. The values of V_f are decreasing in trend (for decreasing X_2) which suggest that there is a specific interaction between the components of the mixtures. An inverse

trend is observed in case of internal pressure as expected. The observed decreasing values of V_f are due to close association between solute and solvent molecules. Similar trends were observed by earlier workers [19, 20].

Similar trend was observed for relaxation time in our dielectric work [21]. Hence the formation of hydrogen bonding between hydroxyl group (-OH) of 2PN and -CH group of hydroxyl benzoates restricts the free internal orientation of the molecules. Gibbs free energy and Helmholtz free energy also showed same trend (Fig. 2) [21]. This trend indicates the presence of interaction between the molecules of the mixture.

The increase in adiabatic compressibility and free length with decreasing concentrations of X_2 indicates significant interactions between Ethyl hydroxyl benzoate and the alkanol molecules forming hydrogen bonding through dipole-dipole interaction.

As alkanols are liquids which are associated through hydrogen bonding and in the pure state they exhibit equilibrium between multimer and monomer species.

The dipole-dipole interaction through hydrogen bonding between Ethyl hydroxyl benzoate and alkanols clearly enhance the decrease in isentropic compressibility and free length. Similar results were observed by earlier workers in their liquid mixtures. Further, the increase in free volume and decrease in internal pressure with rise in concentrations of X_2 in all the systems clearly show the increasing magnitude of interactions [22].

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Project No.: ERIP/ER/0703688/M/01/1134, dated 31-03-2010 of DRDO and UGC DRS LEVEL III program No.F.530/1/DRS/2009 (SAP-I), dated 09-02-2009 New Delhi, to the department of Physics, ANU for providing financial assistance.

REFERENCES

- [1] Sheshagiri Rao MG. Indian J Pure Appl Phys 1971; 9: 169-174.
- [2] Sheshagiri K and Reddy KC. Acustica (Germany) 1973; 29: 59-65.
- [3] Ramamoorthy K and Varadachari PS. Indian J pure Appl phys 1973; 11: 238-242.
- [4] Kaulgud MV and Patil KJ. Indian J pure Appl Phys 1975; 13: 322-324.
- [5] Tiwari V and Pandey JD. Indian J Pure Appl Phys 1980; 18: 51-57.
- [6] Satya Narayanamurthy M. Current science 1964; 33: 364-365.
- [7] Soitkar VS and Jajoo SN. Acoust Lett 1984; 7(12):1991-1998.
- [8] Suryanarayana CV. J Acoust Soc Ind 1983; 13: XI.
- [9] Fletcher A. J Phys Chem 1969; 73: 2217-2225.
- [10] Pimental GC and Maclellan AL. The Hydrogen bond, (WH Freeman and Co, SanFrancisco) 1960.
- [11] Hobbs ME and Bates WW. J Am Chem Soc 1952; 74: 746-749.
- [12] Lin W and Tsay SJ. J Phys Chem 1970; 74: 1037-1041.
- [13] Manisha Gupta and Shukla JP. Indian J Pure Appl Phys 1996; 34: 769-772.



- [14] Pandey J D Rai R D Shukla A K and Misra N. Indian J pure Appl Phys 1993; 31: 84-91.
- [15] Pankaj and Sharma C. Ultrasonics 1991; 29: 344-347.
- [16] Velmourougane S, Nambinarayanan TK, Srinivasa Rao A and Krishnan B. Indian J Phys 1987; 61B: 105-109.
- [17] Jacobson B. Acta Chem Scaud 1952; 6: 1485-1498.
- [18] Eyring H and Kincaid JF. J Chem Phys 1938; 6: 620-629.
- [19] Thirumaran S, Earnest Jayakumar J. Indian J pure Appl Phys 2009; 47: 265-272.
- [20] Rama Rao GV, Viswanadha Sarma A, Ramachandran D and Rambabu C. Indian J pure Appl Phys 2005; 43: 602-608.
- [21] Kumara Sastry SV, Sreehari Sastry S and Murthy VRK. E- J Chem 2012 (in press).
- [22] Ali A, Nain AK. J Pure Appl Ultrason 2000; 22: 10-15.