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MOLECULAR INTERACTION STUDIES ON SOME BINARY ORGANIC LIQUID MIXTURES AT 303K

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ABSTRACT

The ultrasonic velocity, density and viscosity have been measured for the binary mixtures of 1-pentanol with carbon tetrachloride, chloroform and dichloromethane at 303K. The experimental data have been used to calculate the acoustical parameters namely adiabatic compressibility, free length, free volume, internal pressure, acoustical impedance, relaxation time and Gibb's energy. The excess values of some of the above parameters have also been evaluated and discussed in the light of molecular interaction present in the mixtures.

Keywords: Ultrasonic Velocity, Acoustic Parameters, Molecular Interaction, 1-Pentanol

INTRODUCTION

Studies involving density and ultrasonic velocity measurements are important for elucidation of different kinds of association, intermolecular interaction and their relative strength in various multi-component liquid systems **[1].** Ultrasonic spectroscopy is an excellent non-destructive technique for probing the structure of materials. The ultrasound waves when applied to liquids give information about molecular motion. This study is a powerful tool in characterizing the various aspects of physico chemical behaviour of liquid mixture and studying the interaction between the liquid mixtures **[2].** The variation of ultrasonic velocity and related acoustical parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components as well as strongly interacting components **[3].** The study of

excess thermodynamic functions such as excess adiabatic compressibility, excess intermolecular free length, and excess viscosity are of considerable interest in understanding the nature of intermolecular interactions in liquid mixtures **[4]**. Excess properties of binary liquid mixtures give more comprehensive information about the structural and interactional aspects of the liquid mixtures. Thermodynamic and acoustic studies of liquid–liquid mixtures have been pursued for a number of years as a means of probing the intermolecular interactions between molecules **[5].**

The present work deals with the ultrasonic velocity and computation of related parameters in binary system of

1 – Pentanol + carbon tetrachloride (System I)

1 – Pentanol + chloroform (System II)

1 – Pentanol + dichloromethane (System III)

at 303 K. For preparing various concentration mixtures, the mole fractions were varied from 0.1 to 0.9.

EXPERIMENTAL TECHNIQUES

All the chemicals namely 1–Pentanol, carbon tetrachloride, chloroform and dichloromethane were obtained from E-Merck and SD Fine Chemicals Ltd., India. These liquids were used without any further purification, but they were dried in a vacuum desiccator before use. The velocity of sound waves was found using an ultrasonic interferometer (Mittal Enterprises, New Delhi) at a fixed frequency of 3MHz with an accuracy of $\pm 2 ms^{-1}$. The density was measured using pycnometer of capacity 5ml and gave an estimated reproducibility of $0.0001 gcm^{-3}$.Viscosity measurements were carried out with an Oswald's viscometer having time of efflux 0.01s and the accuracy was found to be $\pm 3x10^{-6} Nm^{-2}s$. Flow time measurements were performed using an automatic viscosity (time) measurement unit with a resolution of ±0.1second.The temperature around the viscometer was maintained within 0.1K in an electronically controlled thermostatic water bath.

THEORY AND CALCULATION

The ultrasonic velocity (U), density (ρ) and viscosity (η) in pure liquids and liquid mixture of various concentrations have been measured at 303K.

Thermodynamic and acoustical parameters such as adiabatic compressibility (β) inter molecular free length (L_f), internal pressure (π_i) and acoustic impedance (Z), were determined using the observed values of

velocity, density and viscosity using respective equations and the Excess values of adiabatic compressibility (β^E), free length (L_f^E), internal pressure (π_i^E) and acoustic impedance (Z^E) were evaluated using the equations given below .

Adiabatic compressibility (β):

The speed of sound (U) and the density of the medium (ρ) using Newton and Laplace equation as

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

Intermolecular free length (L_f)

The free length (L_f) is the distance between the surfaces of the neighboring molecules and is given by the equation

$$L_f = K_T \beta^{½} \qquad (2)$$

where K_T is the temperature dependent constant.

Internal pressure (π_i)

The final equation for the evaluation of internal pressure can be obtained by

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

K is a constant, T is the absolute temperature, η is the viscosity in Nsm^{-2}, U is the ultrasonic velocity in ms^{-1}, ρ is the density in Kgm^{-3} of the liquid. The experimental error in the determination of π_i is ± 5%. The cubic packing factor is taken to be 2.

Acoustic Impedance (Z)

The acoustic impedance is the product of the velocity of ultrasound in a medium (U) and its density (ρ) which can be calculated by the relation.

$$Z = U\rho \qquad (4)$$

Where U and ρ are velocity and density of the liquids respectively.

Excess Values (A^E)

In order to study the non-ideality of the liquid mixtures, the difference between the parameters of the real mixtures (A_{exp}) and those corresponding to an ideal mixture (A_{id}) values, namely excess parameters (A^E) of all the acoustic parameters were computed by the relation

$$A^E = A_{exp} - A_i \qquad (5)$$

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

RESULTS AND DISCUSSION:

The experimental values of density, viscosity and ultrasonic velocity for the binary systems I, II and III are listed in **Table 1**. The thermodynamic parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f), Internal pressure (π_i), acoustic impedance (z), relaxation time (τ) and Gibb's

energy (ΔG*) of the three systems are given in the **Tables 2-4**. The excess values of adiabatic compressibility, free length, free volume, internal pressure, acoustic impedance, ultrasonic velocity and viscosity for all the three systems at 303 K are plotted in the **Figures 1 to 7**. From the **Table 1**, it is observed for all the three systems, the velocity and viscosity of the binary liquid mixtures are increasing with increasing mole fraction of 1-pentanol, whereas the density of all the three systems decreases with increasing mole fractions of 1-pentanol. The increase in ultrasonic velocity with increase in concentration of 1-pentanol indicates that there is a dipole-induced dipole interaction between component molecules **[6]**. It is observed from the Tables 2 to 4 that the adiabatic compressibility and free length decreases with increase in mole fraction of 1-pentanol for all the three systems. The adiabatic compressibility is a powerful thermodynamic parameter in sensing the molecular interactions in liquid mixtures **[7].** The addition of 1-pentanol with the $CC1_4$, $CHCl_3$ and CH_2Cl_2 leads to a compact structure due to the presence of dipolar interaction, which contributes to a decrease in free length and compressibility. Further the adiabatic compressibility shows an inverse behavior compared to the ultrasonic velocity in all the systems.

According to the view proposed by Eyring & Kincaid **[8]** as a result of mixing of component liquids the ultrasonic speed increases with decrease in free length & vice versa. The regular fall in free length with the mole fraction of 1-pentanol may be attributed to the close approach of the molecules **[9]**.

From the **Figures 3** and **4**, it is noted that the free volume (V_f) decreases as the concentration of 1-pentanol increases, whereas the internal pressure (π_i) increases due to the various degree of dispersive interaction and the columbic interaction existing between the component molecule **[10]**.

The acoustic impedance (z) **(Figure 5)** decreases with increasing mole fraction of 1-pentanol. When an acoustical wave travels in a medium, there is a variation of pressure from particle to particle. The ratio of the instantaneous pressure excess at any particle of the medium to the instantaneous velocity of that particle is known as "acoustic impedance". The decrease in acoustic impedance with increase in mole fraction indicates significant interaction between the component molecules. This is in agreement with the results of Anwar Ali **[11].**

From the **Tables 2-4**, it is evident that the relaxation time (τ) and Gibbs's energy (ΔG^*) increases with increasing mole fraction of 1-pentanol. The increase in relaxation time is due to structural relaxation process, which shows the presence of molecular interaction between the component molecules. The increase in Gibb's function indicates that the need for longer time for the co-operative process or the rearrangement of molecules in the mixtures, which increases the energy that leads to dissociation

The excess adiabatic compressibility (β^E) and excess free length (L_f^E) are positive **(Figures 1, 2)**. The values of the excess function β^E, L_f^E depends upon several physical and/or chemical contributions. The physical contribution consists of dispersion forces or weak dipole-dipole interaction that leads to positive values β^E and L_f^E. Another factor, which involves a physical contribution, is the geometrical effect allowing the fitting of molecules of two different sizes into each other's structure resulting in negative β^E and L_f^E values. Chemical contributions include breaking up of the associates present in pure liquids, resulting in positive β^E and L_f^E. As we mentioned earlier, positive values of β^E and L_f^E are mainly due to the weak interaction between the component molecules in the mixtures **[12]**.

From the **Figures 3** and **4**, it is observed that the excess free volume (V_f^E) and excess internal pressure (π_i^E) are negative over the entire range of mole fractions in all the systems. Fort and Moore **[13]** noticed that the negative excess values of these function indicate the decrease in strength of interaction between the unlike molecule. The negative sign of excess internal pressure (π_i^E) shows the presence of weak interaction **[14], [15]**. The excess acoustic impedance (Z^E) is positive **(Figure 5)** for lower mole fraction whereas, on increasing the concentration of 1-pentanol Z^E changes from positive to negative. An increasingly negative value of Z^E with mole fraction is indicative of the decreasing strength of interactions between component molecules of the mixture **[16]**.

The observed excess viscosities (η^E) are negative (Fig.7) for all the systems (except in 0.9 mole fraction of 1-pentanol in system – III) over the concentration range investigated. The negative η^E values indicate the weakening of intermolecular interaction between the component molecules [**17], [18].**The negative value of π_i^E and η^E, indicate that only dispersion and dipolar

forces are operating with complete absence of specific interaction **[19].**

From the **Figure 6**, it is observed that the excess ultrasonic velocity (U^E) for all the three binary liquid mixtures is negative (except in 0.9 mole fraction of 1-pentanol in system – III). The negative value for U^E indicates the decrease in the strength of interaction between the molecules Negative deviations in η^E and U^E from linear dependence suggest the presence of weak interaction between the component molecules **[20]**.

The behaviour of η^E and U^E both being negative over the whole range of mole fraction, support each other.

Table 1: Values of Density (ρ), Viscosity (η) and Velocity (U) of system – I to III

Mole fraction		System I			System II			System III		
X_1	X_2	ρ kg m^{-3}	η x 10^3 Nsm^{-2}	U ms^{-1}	ρ kg m^{-3}	η x 10^3 Nsm^{-2}	U ms^{-1}	ρ kg m^{-3}	η x 10^3 Nsm^{-2}	U ms^{-1}
0.0999	0.8999	1447.01	0.9216	0911.72	1309.10	0.6474	0970.32	1153.77	0.5334	1031.68
0.1999	0.7999	1379.10	0.9914	0935.03	1262.80	0.7130	0988.96	1127.09	0.5917	1043.98
0.2999	0.6999	1308.47	1.0670	0960.52	1216.26	0.8361	1010.04	1083.95	0.7648	1065.08
0.3999	0.5999	1239.79	1.3064	0987.04	1150.12	0.9827	1040.56	1033.04	0.9403	1092.28
0.4999	0.4999	1164.61	1.4032	1021.08	1082.36	1.1420	1075.65	0990.13	1.0491	1119.12
0.5999	0.3999	1091.17	1.5578	1060.32	1023.70	1.3957	1107.48	0945.42	1.2342	1146.04
0.6999	0.2999	1020.82	1.7981	1101.00	0964.89	1.6762	1143.36	0908.13	1.5784	1170.00
0.7999	0.1999	0940.92	2.1017	1149.56	0922.89	2.0075	1169.64	0871.83	1.8356	1195.8
0.8999	0.0999	0878.43	2.4137	1196.52	0858.79	2.3623	1216.98	0837.79	2.3394	1228.08

Table 2: Values of Adiabatic compressibility (β), Free length (L_f), Free volume (V_f), Internal pressure (π_i), Acoustic Impedance (z), Relaxation time (τ) and Gibb's energy (ΔG*) of system – I at 303 K

Mole fraction		β x 10^{10} Pa^{-1}	L_f x 10^{10} m	V_f x 10^7 m^3 mol^{-1}	π_i x 10^{-6} Nm^{-2}	Z x 10^5 Kgm^2 s^{-1}	τ x 10^{13} s	ΔG* x 10^{21} KJ mol^{-1}
X_1	X_2							
0.0999	0.8999	8.314	0.5753	1.985	396.1	13.19	10.22	7.794
0.1999	0.7999	8.294	0.5746	1.726	414.3	12.89	10.96	8.089
0.2999	0.6999	8.284	0.5743	1.498	433.0	12.57	11.78	8.392
0.3999	0.5999	8.279	0.5741	1.068	483.5	12.24	14.42	9.236
0.4999	0.4999	8.236	0.5726	0.9326	502.6	11.89	15.41	9.513
0.5999	0.3999	8.151	0.5697	0.7759	531.0	11.57	16.93	9.907
0.6999	0.2999	8.081	0.5672	0.6059	573.8	11.24	19.37	10.47
0.7999	0.1999	8.042	0.5658	0.4655	618.7	10.82	22.54	11.10
0.8999	0.0999	7.952	0.5626	0.3632	671.3	10.51	25.59	11.63

Table 3: Values of Adiabatic compressibility (β), Free length (L_f), Free volume (V_f), Internal pressure (π_i), Acoustic Impedance (z), Relaxation time (τ) and Gibb's energy (ΔG*) of system – II at 303 K

Mole fraction		β x 10^{10} Pa^{-1}	L_f x 10^{10} m	Vf x 10^7 m^3 mol^{-1}	π_i x 10^{-6} Nm^{-2}	Z x 10^5 Kgm^2 s^{-1}	τ x 10^{13} s	ΔG* x 10^{21} KJ mol^{-1}
X_1	X_2							
0.0999	0.8999	8.113	0.5683	2.597	396.6	12.70	7.003	6.215
0.1999	0.7999	8.097	0.5678	2.219	415.5	12.49	7.697	6.610
0.2999	0.6999	8.059	0.5664	1.730	448.6	12.28	8.984	7.257
0.3999	0.5999	8.030	0.5654	1.359	477.4	11.97	10.52	7.917
0.4999	0.4999	7.985	0.5638	1.091	503.2	11.64	12.16	8.522
0.5999	0.3999	7.964	0.5631	0.8057	547.4	11.34	14.82	9.350
0.6999	0.2999	7.928	0.5618	0.6125	588.9	11.03	17.72	10.10
0.7999	0.1999	7.920	0.5615	0.4605	642.5	10.79	21.20	10.85
0.8999	0.0999	7.862	0.5595	0.3640	677.3	10.45	24.76	11.50

Table 4: Values of Adiabatic compressibility (β), Free length (L_f), Free volume (V_f), Internal pressure (π_i) Acoustic Impedance (z), Relaxation time (τ) and Gibb's energy (ΔG*) of system – III at 303 K

Mole fraction		$\beta \times 10^{10}$ Pa^{-1}	$L_f \times 10^{10}$ m	$V_f \times 10^7$ m^3 mol^{-1}	$\pi_i \times 10^{-6}$ Nm^{-2}	$Z \times 10^5$ Kgm^2 s^{-1}	$\tau \times 10^{13}$ s	$\Delta G^* \times 10^{21}$ KJ mol^{-1}
X_1	X_2							
0.0998	0.8999	8.143	0.5694	2.390	460.9	11.90	5.791	5.420
0.1999	0.8001	8.141	0.5693	2.095	472.9	11.77	6.422	5.853
0.2999	0.6999	8.133	0.5690	1.477	516.4	11.54	8.293	6.922
0.3999	0.5999	8.114	0.5683	1.132	545.2	11.28	10.17	7.776
0.4999	0.4999	8.064	0.5666	1.001	550.7	11.08	11.28	8.208
0.6000	0.3999	8.053	0.5662	0.8180	569.8	10.83	13.25	8.882
0.6999	0.2999	8.044	0.5659	0.5866	618.3	10.63	16.93	9.906
0.7999	0.1999	8.021	0.5651	0.4859	639.0	10.43	19.63	10.53
0.8999	0.0999	7.914	0.5613	0.3535	690.3	10.29	24.69	11.48

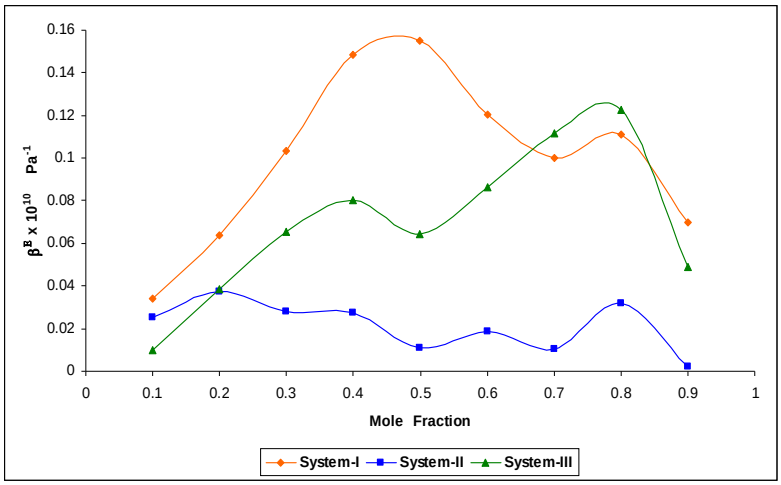

Figure 1: Excess Adiabatic compressibility Vs mole fraction for the Systems I-III at 303K

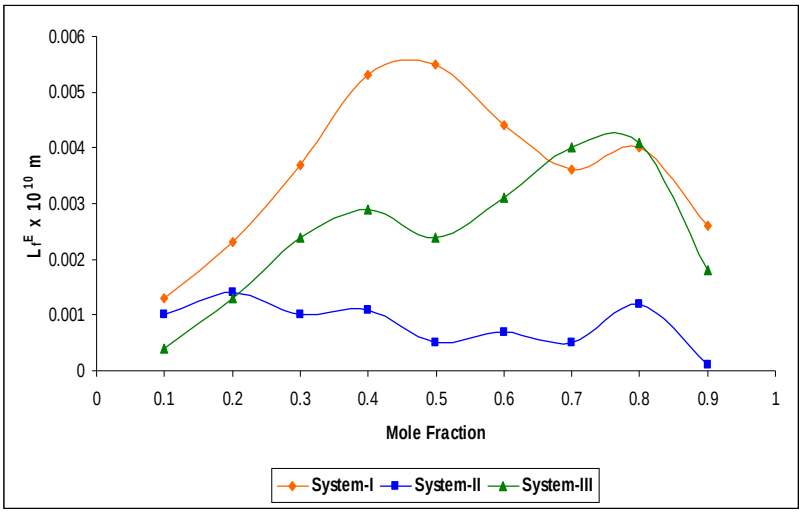

Figure 2: Excess Free length Vs mole fraction for the Systems 1 – III at 303 K

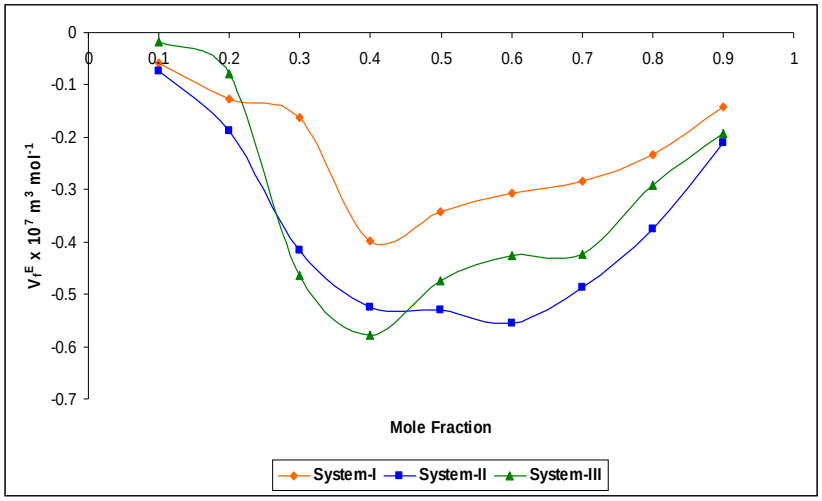

Figure 3: Excess Free volume Vs. Mole fraction for the System I – III at 303 K

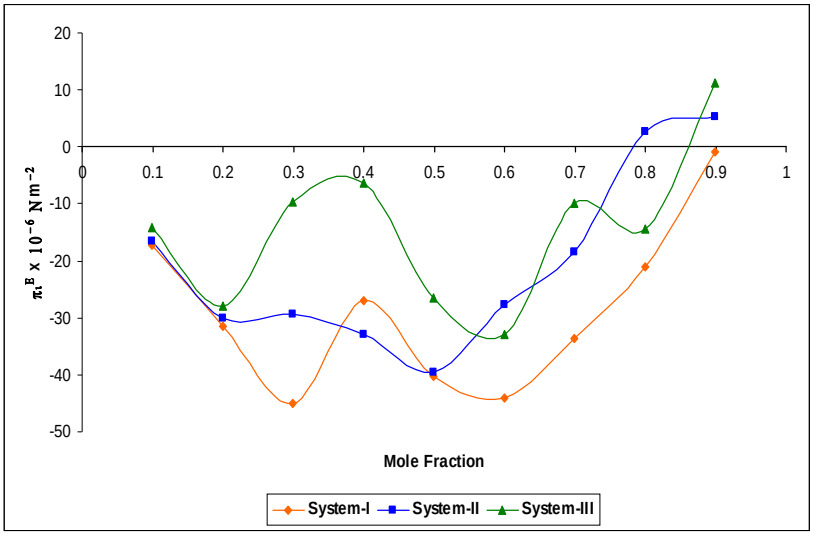

Figure 4: Excess Internal pressure Vs. Mole fraction for the System I – III at 303 K

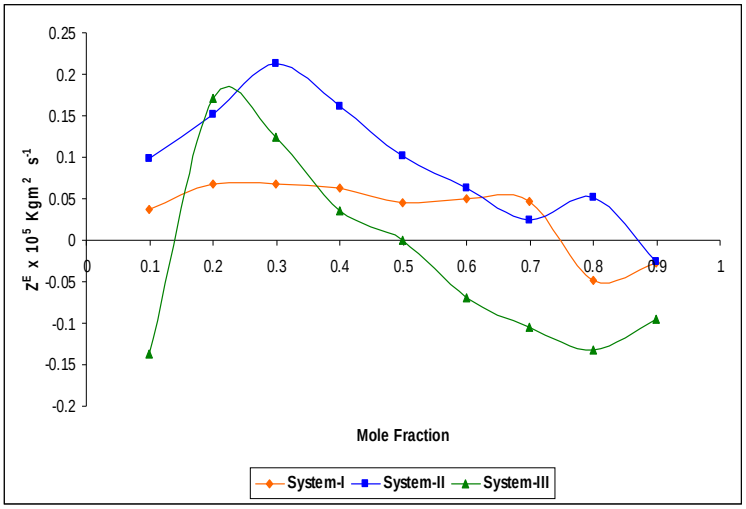

Figure 5: Excess Acoustic Impedance Vs. Mole fraction for the System I – III at 303 K

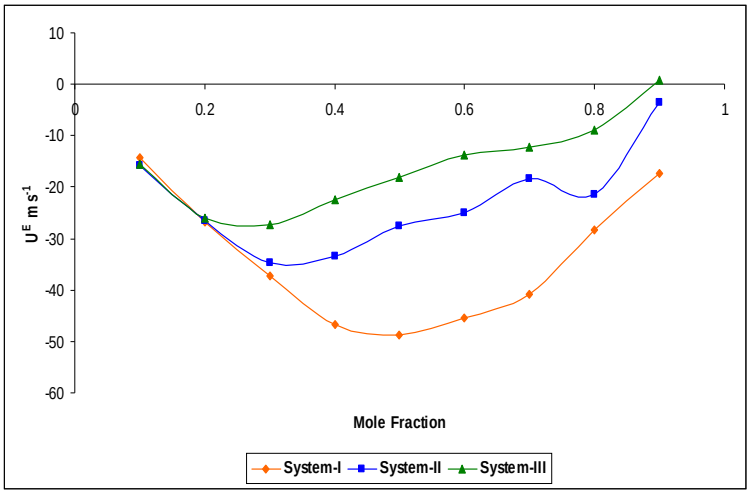

Figure 6: Excess Ultrasonic Velocity Vs. Mole fraction for the System I – III at 303 K

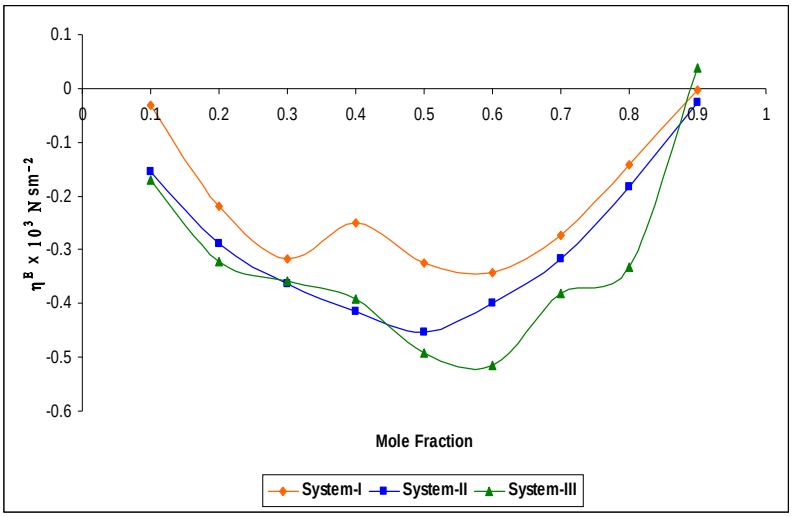

Figure 7: Excess Viscosity Vs. Mole fraction for the System I – III at 303 K

CONCLUSION

From the present study, it may be concluded that the variation in the acoustic parameters, the sign and extent of deviation of the excess function derived from the ultrasonic velocity density and viscosity suggest the presence of molecular interaction between the component of molecules in the binary liquid mixtures. The positive values of β^E, L_f^E and the negative values of V_f^E, π_i^E η^E and U^E in all the three systems reveals the presence of weak dipolar and dispersive interaction between the component molecules in the mixtures. The conclusions highlight the importance of ultrasonic method in detecting weak molecular interaction between the component molecules of the mixtures.

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