Ultrasonic Studies on Binary Mixtures of Acetyl Acetone at 301K

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Abstract: The ultrasonic velocity (U), density (ρ) and viscosity (η) measurements have been carried out for the binary mixtures of acetyl acetone with benzene, carbon tetra chloride and isoamyl alcohol at 301 K. From the measured values of ultrasonic velocity, density and viscosity, parameters such as internal pressure (π_i), free volume (V_f) and acoustical parameters such as adiabatic compressibility (β), inter molecular free length (L_f), acoustic impedance (Z), relaxation time (τ) have been calculated. The results have been analyzed and interpreted in terms of molecular interactions.

Introduction

Ultrasonic methods find extensive applications for characterizing aspects of physicochemical behaviour such as the nature of molecular interactions in pure liquids as well as liquid mixtures. The thermodynamic functions of binary liquid mixtures provide insight into the structure breaking and making effect of the component liquids. Derived parameters such as internal pressure and free volume studies will be useful to know the molecular interactions of the systems. Ultrasonic velocity is one of the important parameters, frequently used to investigate intermolecular interactions in binary liquid mixtures[1-4]. Ultrasonic velocity measurements have been successfully employed to detect and assess weak and strong molecular interactions, present in binary[5,6] and ternary[7,8] liquid mixtures. In this paper, an attempt to investigate the ultrasonic studies of acetyl acetone in benzene, carbon tetrachloride, isoamyl alcohol binary liquid mixture systems at 301 K are made. We have measured density (ρ), ultrasonic velocity (U), viscosity (η) of mixtures of acetyl acetone + benzene, + carbon tetra chloride, + isoamyl alcohol with different mole fractions at a temperature of 301 K. From this data, acoustical parameters like adiabatic

compressibility (β), Inter molecular free length (L_f), Acoustic impedance (Z), Relaxation time (τ) are computed. Results are used to explain the nature of molecular interactions between mixing compounds.

Experimental

All the chemicals used in present work were analytical reagent (AR) grade (99.9% pure) and were supplied by SD fine chemicals Ltd, Bombay, India and Qualigens chemicals, India. The liquids were thoroughly distilled to remove dissolved impurities using standard chemical procedures[9]. The purity of the samples was checked by the density measurements and the results were compared with the literature values. Ultrasonic velocities were measured with ultrasonic interferometer (model F80) supplied by Mittal enterprises, New Delhi, operating at a frequency of 2 MHz. It has an accuracy of ±0.1%. Viscosities of pure compounds and their mixtures were determined using Ostwald's viscometer with an accuracy of ±0.002%, calibrated with double distilled water. The densities of pure compounds and their solutions were measured accurately using 10 mL specific gravity bottles in Dhona electric balance precisely and the accuracy in weighing is ±0.1 mg. Acoustic parameters such as adiabatic compressibility (β), acoustic impedance (Z), relaxation time (τ), free length (L_f), internal pressure (π_i) and free volume (V_f) were determined using the following relations[10].

$$\beta = \frac{1}{U^2 \rho} \tag{1}$$

$$L_f = K_T \beta^{1/2} \tag{2}$$

$$V_f = \left[\frac{M_{eff} U}{\eta K} \right]^{3/2} \tag{3}$$

$$\pi_i = bRT \left[\frac{K\eta}{U} \right] \left[\frac{\rho^{2/3}}{\left(M_{eff} \right)^{7/6}} \right] \tag{4}$$

$$Z = \rho U \tag{5}$$

$$\tau = \frac{4\eta}{3\rho U^2} \tag{6}$$

Where K_T is the temperature dependent constant having a value of 199.53×10^{-8} in MKS system, K is temperature independent constant whose value is 4.28×10^9 in MKS system, b is a factor depending on packing pattern which is 1.78, R is the gas constant and T is temperature in K, η is the viscosity in pascals, U is ultrasonic velocity in m/s, ρ is the density in Kg/m^3 and M_{eff} is the effective molecular weight, given by $M_{eff} = \Sigma x_i m_i$ where x is the mole fraction and m is the molecular weight of the ith component.

Results and Discussion

The binary mixture systems taken up for the present study are: acetyl acetone + benzene (I), acetyl acetone + carbon tetra chloride (II) and acetyl acetone + isoamyl alcohol (III). The experimentally determined values of velocity, density and viscosity along with the calculated values of internal pressure (π_i), free volume (V_f), adiabatic compressibility (β), free length (L_f), acoustic impedance (Z) and relaxation time (τ) for all the systems at 301 K are reported in Table 1.

Table 1. Velocity (U), density (ρ), viscosity (η), internal pressure (π_i), free volume (V_f), adiabatic compressibility (β_s), free length (L_f), acoustic impedance (Z) and relaxation time (τ) of binary liquid systems I, II and III at 301 K.

System I: Acetyl acetone + benzene

X_1	U ms^{-1}	$\rho \times 10^3$ kg m^{-3}	ηPa	$\pi_i \times 10^6$ Pa	$V_f \times 10^{-8}$ m^{3}mol^{-1}	$\beta_s \times 10^{-10}$ kg^{-1}ms^2	$L_f \times 10^{-10}$ m	$Z \times 10^3$ kg m^{-2}s^{-1}	$\tau \times 10^{-12}$ s
0.0000	1260.0	0.8722	0.6167	3.6399	0.2277	7.2217	0.5362	1099.0	113.8651
0.0797	1262.1	0.8737	0.6188	3.5575	0.2347	7.1865	0.5348	1112.6	114.8223
0.1631	1264.6	0.8930	0.6224	3.5230	0.2413	7.0897	0.5312	1123.8	118.4158
0.2505	1266.3	0.8950	0.6248	3.4370	0.2491	6.9712	0.5268	1133.1	119.5044
0.3421	1268.0	0.9052	0.6373	3.3984	0.2511	6.8709	0.5230	1147.8	123.6801
0.4382	1270.5	0.9143	0.6505	3.3579	0.2533	6.7808	0.5195	1161.2	127.9090
0.5392	1272.4	0.9183	0.6604	3.2926	0.2577	6.7174	0.5171	1172.1	130.8520
0.6454	1274.7	0.9346	0.6735	3.2629	0.2593	6.5922	0.5122	1190.7	136.2377

System II: Acetyl acetone + carbon tetra chloride

X_1	Ums^{-1}	$\rho \times 10^3$ kg m^{-3}	η Pa	$\pi_i \times 10^6$ Pa	$V_f \times 10^{-8}$ m^{3}mol^{-1}	$\beta_s \times 10^{-10}$ kg^{-1}ms^2	$L_f \times 10^{-10}$ m	$Z \times 10^3$ kg m^{-2} s^{-1}	$\tau \times 10^{-12}$ s
0.0000	893.0	1.6279	1.0416	3.8620	0.1710	7.7031	0.5538	1453.7	180.2896
0.1458	931.7	1.6259	1.0415	3.8013	0.1725	7.0852	0.5311	1514.8	196.0021
0.2626	970.4	1.6188	1.0257	3.7196	0.1736	6.5598	0.5110	1570.9	208.4877
0.3790	1009.1	1.6137	1.0095	3.6628	0.1740	6.0853	0.4922	1628.4	221.1971
0.4870	1047.8	1.6107	0.9995	3.6092	0.1758	5.6548	0.4745	1687.7	235.6723
0.5875	1086.5	1.6026	0.9989	3.5069	0.1762	5.2857	0.4587	1741.2	251.9730
0.6811	1125.2	1.5945	0.9831	3.4165	0.1775	4.9534	0.4441	1794.1	264.6328
0.7687	1163.9	1.5783	0.9752	3.3675	0.1788	4.6771	0.4315	1836.9	278.0058

System III: Acetyl acetone + isoamyl alcohol

X_1	Ums^{-1}	$\rho \times 10^3$ kg m^{-3}	ηPa	$\pi_i \times 10^6$ Pa	$V_f \times 10^{-8}$ m^{3}mol^{-1}	$\beta_s \times 10^{-10}$ kg^{-1}ms^2	$L_f \times 10^{-10}$ m	$Z \times 10^3$ kg m^{-2} s^{-1}	$\tau \times 10^{-12}$ s
0.0000	1210.0	0.8109	3.0606	6.8408	0.0232	8.4224	0.5791	981.2	484.5138
0.0891	1217.1	0.8291	2.0079	5.5376	0.0449	8.1426	0.5694	1009.1	328.7995
0.1803	1224.4	0.8565	1.4125	4.6579	0.0781	7.7925	0.5570	1048.4	241.6944
0.2739	1231.3	0.8663	1.2912	4.4074	0.0919	7.6588	0.5522	1060.6	224.7999
0.3698	1238.7	0.8758	1.1636	4.1449	0.1103	7.4497	0.5446	1084.2	208.2728
0.4681	1245.0	0.8879	1.0650	3.9333	0.1295	7.2653	0.5378	1105.5	195.4477
0.5690	1252.8	0.9042	0.9274	3.6540	0.1639	7.0554	0.5300	1132.0	175.2680
0.6725	1259.2	0.9205	0.8847	3.5487	0.1809	6.8532	0.5223	1158.9	172.1346

Figure 1-6 represents the variation of internal pressure (π_i), free volume (V_f), adiabatic compressibility (β), free length (L_f), acoustic impedance (Z) and relaxation time (τ) with mole fraction for all the systems I, II and III respectively.
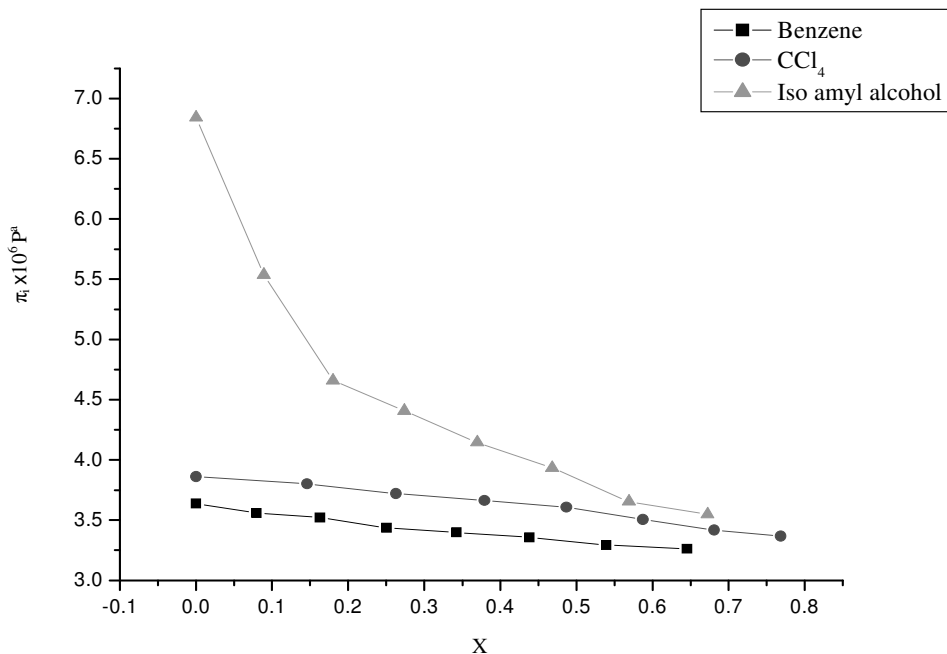
Figure 1. Variation of internal pressure (π_i), with mole fraction for all the systems
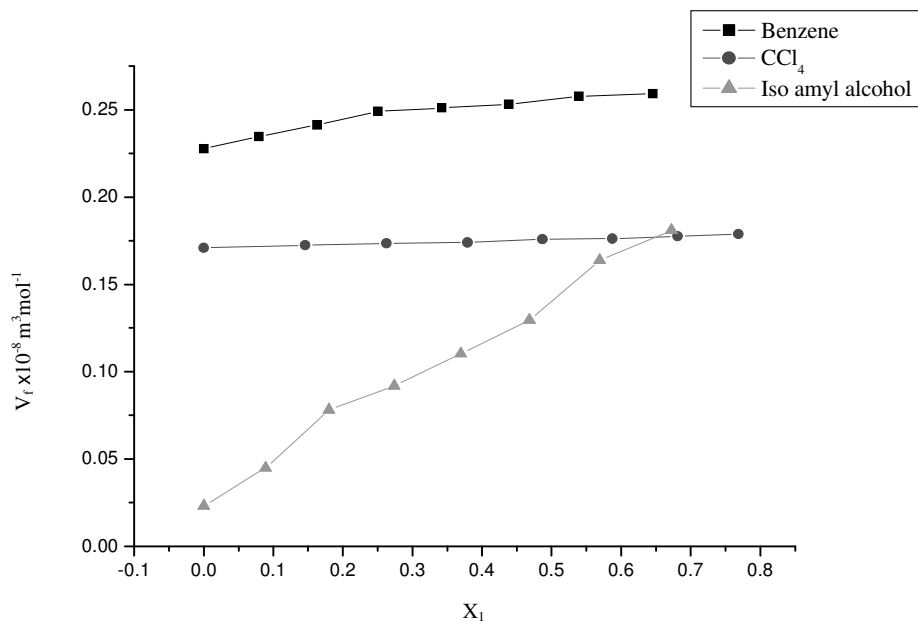
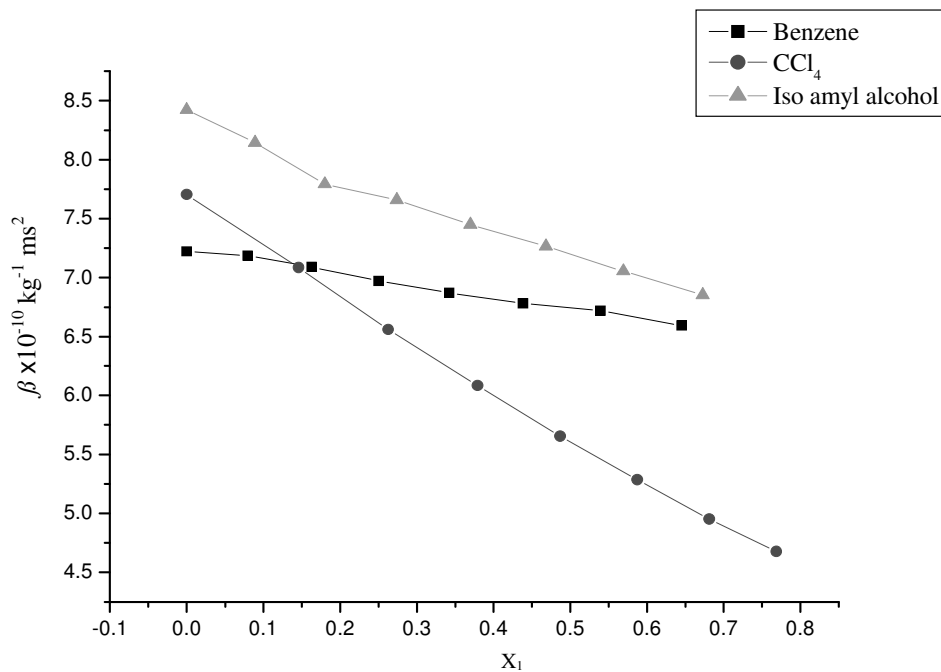**Figure 2.** Variation of free volume (V_f), with mole fraction for all the systems

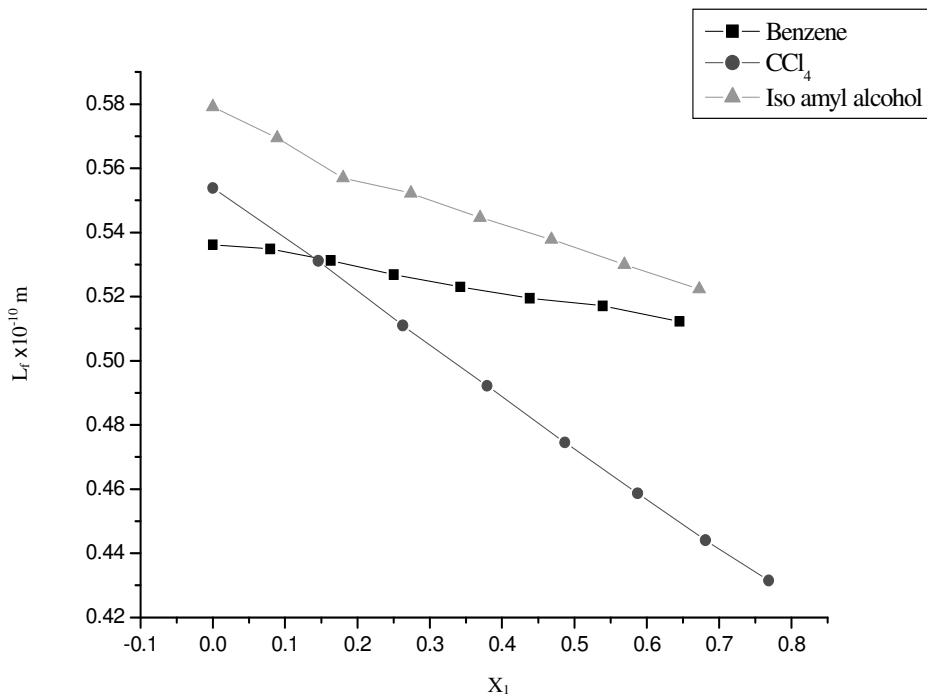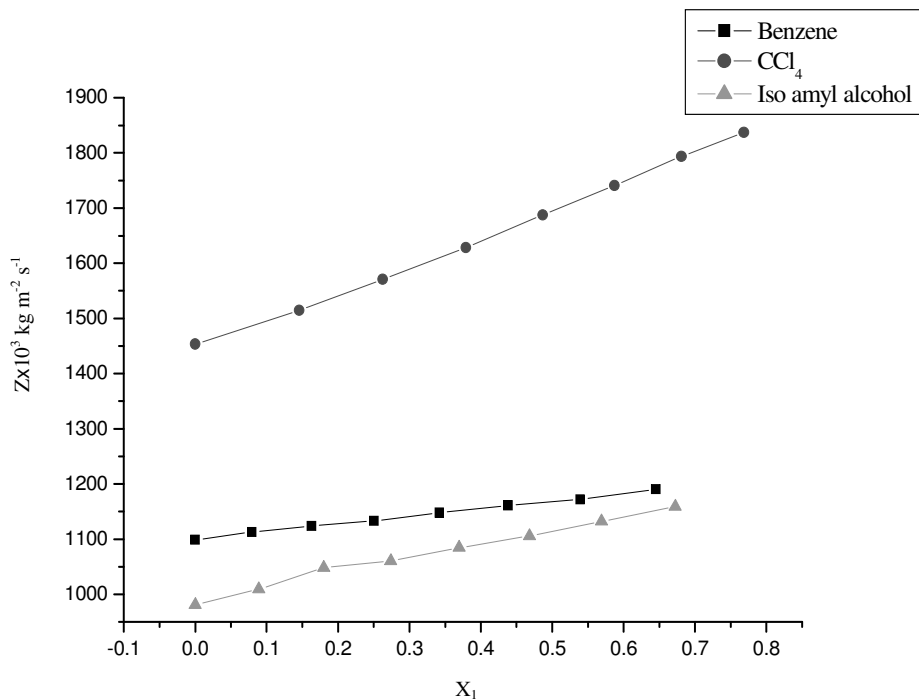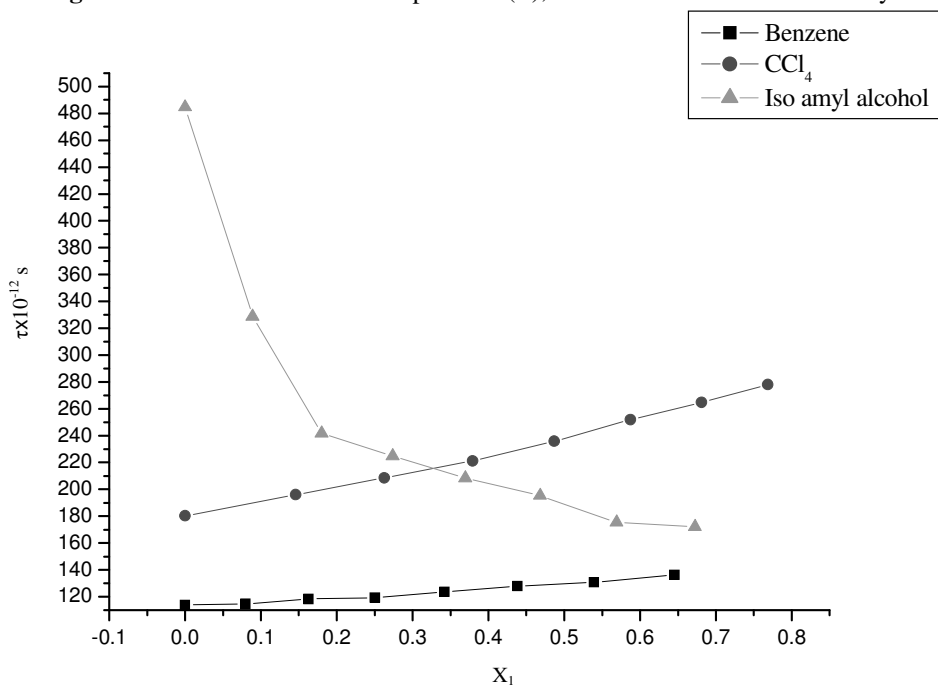**Figure 3.** Variation of adiabatic compressibility (β), with mole fraction for all the systems

Figure 4. Variation of free length (L_f), with mole fraction for all the systems

Figure 5. Variation of acoustic impedance (Z), with mole fraction for all the systems

Figure 6. Variation of relaxation time (τ), with mole fraction for all the systems

In all the three binary systems, the ultrasonic velocity increases with increasing concentration of acetyl acetone. The variation of ultrasonic velocity in a solution depends upon the increase or decrease of intermolecular free length after mixing the components. Based on the model for sound propagation proposed by eyring and kincaid[11], ultrasonic velocity should increase, if the inter molecular free length decreases and vice verse. This fact was noticed in the present study for all the three binary liquid systems. Same trend was noticed by earlier workers[12] in their liquid mixtures.

In system I, benzene is a non polar liquid and as the concentration of acetyl acetone increases there will be induced polarization in the benzene molecule and this result in molecular association. In fact, the molecular association increases ultrasonic velocity (U) and acoustic impedance (Z), decreases intermolecular free length (L_f) and adiabatic compressibility (β). A reduction in adiabatic compressibility (β) is an indication that component molecules are held close to each other. The decrease in the values of adiabatic compressibility ($β_s$) and inter molecular free length (L_f) with increase in ultrasonic velocity (U) further strengthens the strong molecular association between the unlike molecules through hydrogen bonding.

In system II, carbon tetra chloride is a non polar liquid and the parameters are expected to show the same trend as in system I. This fact is reflected clearly from the values of ultrasonic velocity (U), intermolecular free length (L_f), adiabatic compressibility ($β_s$) and acoustic impedance (Z) for system II.

Alcohols usually exist in polymeric form. In the presence of polar molecules, they dissociate into monomers. In system III, both the components are polar and there is tendency for internal hydrogen bonding in acetyl acetone. With the increase of isoamyl alcohol, the tendency for intermolecular hydrogen bonding increases. The association is stronger and we expect a larger variation in the parameters. Eventually ultrasonic velocities (U) of both the components are nearly equal. In system III, this fact is reflected in increase of ultrasonic velocity (U) and hence decrease in inter molecular free length (L_f) also it can be observed that adiabatic compressibility (β) values decrease with increasing concentrations of isoamyl alcohol. Similar results were obtained by earlier workers[12-14] in their liquid mixtures.

Acoustic impedance (Z) of a material is the opposition exerted by the medium to displacement of the medium's particles by the sound energy. It is important to measure acoustic impedance because studies have shown that in solvent mixtures when molecular interactions occurs, acoustic impedance exhibits a non-linear variation with increasing mole fraction of solute. It has been found that the acoustic impedance gives a peak in conjunction with ultrasonic velocity maxima and isentropic compressibility minima. This was used as an essential tool to predict molecular level interactions in binary and ternary liquid mixtures. In systems I and III, Acoustic impedance (Z) showed increasing trend while it showed decreasing trend in system II.

The parameter relaxation time (τ) was increasing in system I and II while it showed a decreasing trend in system III. The relaxation time of binary liquid mixtures is always much greater than either of the polar solutes in the inert solvent[15].

Further, the increase in free volume (V_f) and decrease in internal pressure ($π_i$) with rise in concentration of acetyl acetone in all the three systems under study, clearly indicate the increasing magnitude of interactions[12,16].

Conclusion

In system I inter molecular association is weak. In system II and III, the molecular associations are stronger due to inter molecular hydrogen bonding.

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