Studies on liquid–liquid interactions of some ternary mixtures by density, viscosity and ultrasonic speed measurements

M. Umadevi [a,*], R. Kesavasamy [b], K. Rathina [c], R. Mahalakshmi [d]

[a] Department of Physics, Sri Parasakthi College for Women, Courtallam, India
[b] Department of Physics, Sri Ramakrishna Engineering College, Coimbatore, India
[c] Department of Physics, Kumaraguru College of Technology, Coimbatore, India
[d] Department of Chemistry, Kumaraguru College of Technology, Coimbatore, India

ARTICLE INFO

ABSTRACT

The density, viscosity and ultrasonic velocity have been measured for the ternary mixtures of Methyl benzoate, cyclohexane with primary alcohol (1-propanol, 1-butanol, 1-pentanol and 1-hexanol) at 303.15, 308.15 and 313.15K. From the measured values, the acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f) have been computed. The excess parameters like excess adiabatic compressibility (β^E), excess free length (L_f^E), excess free volume (V_f^E) and excess internal pressure (π_i^E) were also calculated in order to investigate the molecular interaction between the components of liquid mixtures.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The measurement of ultrasonic speed enables the accurate determination of some useful acoustical and thermodynamic parameters and their excess functions, which are highly sensitive to molecular interactions in liquid mixtures [1,2].

The nature and relative strength of the molecular interaction between the components of the liquid mixtures have been successfully investigated by the ultrasonic method by Ali et al. [1] and Kannappan and Palani [3]. These interactions helps in better understanding the nature of the solute and solvent i.e., whether the solute modifies or distorts the structure of the solvent. The structure, nature and prevailing conditions of the solvents and solutes, play an important role on resulting properties and interactions occurring in the solution.

The compositional and temperature dependence of thermodynamic properties have proved by Satyanarayan Rao et al. [4] and it was a very useful tool in understanding the nature and extent of pattern of molecular aggregation resulting from intermolecular interactions between components. Ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules and has been

adequately employed in understanding the nature of molecular interaction in binary and ternary mixtures (Rai et al. [5]; Nikam et al. [7]; Peralta et al. [8]; Resa et al. [9]Nikam and Kharat [6]; Prasad et al. [10], [11]; Oswal et al. [12]).

Systematic studies of various relations have been made for binary liquid mixture, multi component liquid mixtures which are of great practical importance in many industrial processes as they provide a wide choice of solutions with appropriate composition and properties. The non-linearity may be explained on the basis of molecular dimensions and the forces acting between the molecules. Ultrasonic velocity together with density and viscosity data furnish a wealth of information about the interaction between ions, dipoles, H-bonding, multipolar and dispersive forces (Eyring and John [13]; Bhadja et al. [14]; Syamala et al. [15] Ramamoorthy et al. [32];Sarkar and Roy [16]).

Compressed liquid density measurements for Methyl benzoate, Cyclohexane or hexanol have been studied by Davila et al. [18]. They found that Methyl benzoate structure is disrupted by the globular shaped Cyclohexane, which is considered as an order destroyer(Prausnitz et al. [17]).

Therefore, in order to have a clear understanding of the intermolecular interactions between the component molecules, the author has performed a thorough study on the molecular interactions using ultrasonic velocity data. The present work deals with the measurement of ultrasonic velocity and computation of related parameters in the following ternary systems,

* Corresponding author at: No. 69, Abbas Garden, 5th Cross, Thadagam road, Luna Nagar, Edayarpalayam (PO), Coimbatore -641025.
  E-mail address: devuma55@gmail.com (M. Umadevi).

Table 1
Values of density (ρ), viscosity (η) and ultrasonic velocity (U) for pure liquids.

Liquids	ρ kg m^{-3}			η × 10^3 N s m^{-2}			U m s^{-1}		
	Temperature (K)								
	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
Methyl benzoate	1078.1	1076.8	1073.6	1.5539	1.4662	1.3374	1346.66	1314.26	1286.99
Cyclohexane	768.80	762.40	757.10	0.80	0.72	0.66	1230.33	1211.55	1290.60
1-Propanol	800.6	794.9	789.5	1.6095	1.4162	1.2517	1193.40	1180.50	1163.65
1-Butanol	805.1	803.2	799.15	2.1604	1.8615	1.6309	1230	1212.1	1198.56
1-Pentanol	806.76	801.78	800.26	2.7656	2.4088	2.0934	1252.9	1241.91	1217.4
1-Hexanol	810.28	807.5	803.12	3.523	3.1814	2.7857	1288.49	1272.5	1255.1

System I: Methyl benzoate+Cyclohexane+1-Propanol
System II: Methyl benzoate+Cyclohexane+1-Butanol
System III: Methyl benzoate+Cyclohexane+1-Pentanol
System IV: Methyl benzoate+Cyclohexane+1-Hexanol

The experimentally determined values of density, viscosity and ultrasonic velocity for all the mixtures for different mole fractions were studied at T303.15, 308.15 and 313.15K. The acoustical and thermo dynamical parameters are calculated using standard equations.

2. Materials and methods

All the chemicals used in the present work are Analar grade. The purity of the chemicals was ascertained by comparing their density, viscosity and ultrasonic velocity at 303.15, 308.15, and 313.15K which agrees with the corresponding literature values. The mixtures of Methyl benzoate, Cyclohexane with primary alcohol (1-propanol,1-butanol, 1-pentanol and 1-hexanol) were prepared by weight. The ultrasonic velocity was measured by a single crystal interferometer with a high degree of accuracy operating at a frequency of 3MHz (model F-05, with digital micrometer) at 303.15, 308.15 and 313.15 K. The viscosity was measured by Ostwald's viscometer. An electronically operated constant temperature water bath was used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. Densities of the mixtures have been found by relative measurement method.

3. Theory and calculations

Intermolecular free length (L_F) is calculated using the standard expression

$$L_F = K\beta^{1/2} \tag{1}$$

where K is a temperature dependent constant known as Jacobson constant and β is the adiabatic compressibility that can be calculated from

the speed of sound (U) and the density of the medium (ρ) as

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

The relation for free volume in terms of ultrasonic velocity (U) and the viscosity (η) of the liquid as

$$V_F = \left(\frac{M_{eff}\, U}{\eta K}\right)^{3/2}. \tag{3}$$

3.1. Excess compressibility

$$\beta_T = \frac{n_1\beta_1 + n_2\beta_2 + n_3\beta_3}{n_1 + n_2 + n_3} \tag{4}$$

where n_1, n_2 and n_3 are the number of moles of the components and β_1, β_2, and β_3 are the compressibilities of the components, and β_T is the compressibility of the ideal mixture. In certain liquid mixtures which deviate from ideal behavior, the experimentally determined compressibility (β_s) will be different from that of calculated adiabatic compressibility (β_T).

3.2. Excess intermolecular free length

$$L_F^E = L_F^{exp} - \left(L_F^A X_A + L_F^B X_B + L_F^C X_C\right) \tag{5}$$

where L_F^A, L_F^B, L_F^C are the intermolecular free length, X_A, X_B, X_C are mole fractions of the components A, B and C, and L_F^{exp} is the experimental intermolecular free length of the mixture.

Table 2
Values of density (ρ), viscosity (η) and ultrasonic velocity (U) for System I: Methyl benzoate (X$_1$)+Cyclohexane (X$_2$)+1-Propanol (X$_3$).

Mole fraction		ρ kg m^{-3}			η × 10^3 N s m^{-2}			U m s^{-1}		
x$_1$	x$_3$	Temperature (K)								
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	957.90	957.00	953.00	0.9344	0.8826	0.8403	1282.80	1270.00	1246.00
0.4886	0.1204	930.00	928.70	926.30	0.9478	0.8956	0.8427	1278.60	1256.40	1227.00
0.3691	0.2419	889.20	886.60	883.00	0.958	0.9053	0.8528	1246.00	1220.00	1207.00
0.3003	0.3457	874.30	874.00	870.80	0.9674	0.9173	0.8653	1231.50	1208.00	1198.80
0.1829	0.4511	846.00	844.50	836.60	0.9977	0.9462	0.8782	1218.60	1197.60	1181.40
0.0893	0.5519	812.60	811.40	802.80	1.0056	0.9551	0.8989	1190.40	1177.00	1148.40
0	0.6491	778.90	775.20	771.30	1.1000	1.0225	0.9392	1174.80	1148.40	1118.00

Table 3
Values of density (ρ), viscosity (η) and ultrasonic velocity (U) for System II: Methyl benzoate (X₁)+Cyclohexane (X₂)+1-Butanol (X₃).

Mole fraction		ρ kg m^{-3}			$\eta \times 10^3$ N s m^{-2}			U m s^{-1}		
x_1	x_3	Temperature (K)								
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	957.90	957.00	953.00	0.9344	0.8826	0.8403	1282.80	1270.00	1246.00
0.4886	0.1204	901.81	900.77	897.59	0.9322	0.8687	0.8166	1361.64	1338.26	1316.07
0.3691	0.2419	876.69	874.81	871.63	0.9573	0.8869	0.8296	1295.60	1244.12	1226.14
0.3003	0.3457	848.81	846.49	841.35	0.9639	0.8884	0.8479	1256.12	1194.90	1184.17
0.1829	0.4511	822.51	820.92	814.21	1.0051	0.9314	0.8889	1224.34	1193.46	1178.00
0.0893	0.5519	815.05	813.00	809.00	1.0561	1.0042	0.9285	1187.70	1172.17	1127.80
0	0.6491	782.46	779.22	774.81	1.1963	1.0830	0.9869	1046.20	1010.89	986.30

3.3. Excess free volume

$$\Delta V = X_1 V_1 + X_2 V_2 + X_3 V_3 - \left(X_1 V_1^0 + X_2 V_2^0 + X_3 V_3^0 \right). \qquad (6)$$

The change in volume ΔV is known as the excess volume, and it may be positive or negative, depending on the nature of interaction between the molecules.

3.4. Excess internal pressure

A liquid undergoing a small isothermal-volume expansion does work against the cohesive forces which cause a change in the internal energy (U). The function $\frac{\partial U}{\partial V}$ is known as the internal pressure (P). From Maxwell's equation of thermodynamics

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \qquad (7)$$

i.e., Internal pressure = Kinetic pressure − External pressure.

The term $\left(\frac{\partial P}{\partial T} \right)_V$ in the equation is called the thermal pressure coefficient, and it is equal to $\frac{\alpha}{\beta}$ where α is the coefficient of thermal expansion, and β is the isothermal compressibility. As $\frac{\alpha}{\beta}$ has a large value, and as such P can be neglected in comparison to $T \left(\frac{\partial P}{\partial T} \right)_V$. Hence the equation reduces to

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V = \frac{T\alpha}{\beta}. \qquad (8)$$

Extensive study of literature shows that the internal pressure in liquid solution seems to be such single factor which varies due to all the interactions of type. It is also known that many properties of ionic solution may be derived in terms of intermolecular forces without appealing to the concepts of electrical charge or ionic radii.

4. Results and discussion

The experimentally measured values of density, viscosity and ultrasonic velocity for all the pure liquids at 303.15, 308.15 and 313.15K are presented in Table 1 and the same for the ternary systems (I–IV) are listed in Tables 2–5. Table 6 represents the values of adiabatic compressibility, intermolecular free length, free volume and internal pressure of the pure components at three different temperatures and the Tables 7–10 summarise those values for ternary liquid mixtures. The excess values of the parameters adiabatic compressibility, intermolecular free length, free volume and internal pressure are given in Tables 11–18.

4.1. Density (ρ), viscosity (η) and ultrasonic velocity (U)

From Tables 2–5 it is clear that in all the four systems the ultrasonic velocity of the ternary liquid mixtures decreases with increasing mole fraction of primary alcohol (1-propanol, 1-butanol, 1-pentanol & 1-hexanol). Further in each mixture when the temperature increases, ultrasonic velocities decreases. On close inspection, it is obvious to say that in all the mixtures increase in temperature, decreases the molecular interactions due to thermal agitation. Similar observations were made by Sridevi et al. [19] and Kerboub and Atik [20] in the investigation of temperature dependence of ultrasonic velocity in certain ternary liquid mixtures. The values show a continuous decrease of velocity with increase of mole fraction of alcohol in all the mixtures chosen. It is due to the net dispersive interactions as observed by Thivagarajan and Palaniappan [21]. From Tables 2–5, it is observed that density decreases with increasing mole fraction of alcohol and viscosity values increase with increasing concentration of alcohol. The decrease in values of density and the increase in value of viscosity, with increase in mole fraction suggest the increase in magnitude of intermolecular interactions, which is reported by Arul and Palaniappan [22].

4.2. Adiabatic compressibility (β)

From Tables 7–10, it is observed that in all the cases, the value of adiabatic compressibility increases with increase in concentration of

Table 4
Values of density (ρ), viscosity (η) and ultrasonic velocity (U) for System III: Methyl benzoate (X₁) +Cyclohexane (X₂)+1-Pentanol (X₃).

Mole fraction		ρ kg m^{-3}			$\eta \times 10^3$ N s m^{-2}			U m s^{-1}		
x_1	x_3	Temperature (K)								
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	957.90	957.00	953.00	0.9344	0.8826	0.8403	1282.80	1270.00	1246.00
0.4886	0.1204	937.96	935.93	932.29	1.1061	0.9975	0.9526	1356.70	1315.30	1301.00
0.3691	0.2419	910.34	904.66	901.01	1.1266	1.0264	0.9584	1326.00	1290.00	1281.00
0.3003	0.3457	878.65	875.84	873.38	1.1385	1.031	0.9779	1296.40	1253.70	1224.40
0.1829	0.4511	853.87	846.60	842.51	1.1437	1.0806	1.0023	1260.90	1234.00	1217.40
0.0893	0.5519	823.00	816.15	813.26	1.2342	1.1112	1.0586	1226.00	1212.00	1188.20
0	0.6491	790.50	787.32	783.61	1.5307	1.4516	1.3271	1214.00	1205.00	1200.00

Table 5
Values of density (ρ), viscosity (η) and ultrasonic velocity (U) for System IV: Methyl benzoate (X_1)+Cyclohexane (X_2)+1-Hexanol (X_3).

Mole fraction		ρ kg m^{-3}			$\eta \times 10^3$ N s m^{-2}			U m s^{-1}		
x_1	x_3	Temperature (K)								
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	957.90	957.00	953.00	0.9344	0.8826	0.8403	1282.80	1270.00	1246.00
0.4886	0.1204	933.90	931.88	930.66	1.0606	0.9913	0.9119	1387.15	1348.45	1313.16
0.3691	0.2419	905.47	901.83	900.60	1.081	1.0104	0.9328	1353.55	1317.27	1297.49
0.3003	0.3457	867.69	864.47	863.63	1.2507	1.1525	1.0879	1311.88	1265.71	1248.32
0.1829	0.4511	848.19	845.79	841.29	1.2719	1.1995	1.1422	1297.49	1245.92	1234.53
0.0893	0.5519	823.41	820.21	814.89	1.5345	1.4309	1.3231	1254.00	1230.34	1200.36
0	0.6491	798.63	794.23	792.14	1.9069	1.7009	1.6299	1229.00	1187.76	1166.56

alcohol and as the temperature increases the adiabatic compressibility values are also increase in all the systems. It is primarily that the compressibility changes with structure which leads to change in ultrasonic velocity. The change in adiabatic compressibility in liquid mixtures indicates that there exist a definite contraction on mixing and the variation may be due to complex formation. The addition of interacting molecules breaks up the molecular clustering of the other releasing several dipoles for the interaction. Thus structural arrangement of molecules results in increasing adiabatic compressibility thereby showing intermolecular interactions. Similar results in some liquid mixtures are also reported by others (Sridevi et al. [19]; Kannappan and Shanthi [23]; Kerboub and Atik [20]; Aravinthraj et al. [24]). At high concentration of alcohol in the mixture, there are a large number of alcohol molecules surrounding the ester molecules. At low concentration of alcohol in the mixtures, there are only a small number of alcohol molecules to enable dipole-dipole interaction through hydrogen bonding with the non-associative ester molecules. The associative alcohol molecules act as proton donor enabling hydrogen bonding with Methyl benzoate molecules (Trenzado et al. [25]).

4.3. Free length (L_f)

The free length of a system is a measure of intermolecular attraction between the components in ternary mixtures. From Tables 7–10, it is observed that the free length increase with the increasing concentration of primary alcohol, and also as temperature increases the free length values are found to be increase. L_f values are almost linear in all the systems. Further, the increase in compressibility brings the molecules closer, resulting in an increase of intermolecular free length.

Intermolecular free length is found to be a predominating factor, which depends upon the adiabatic compressibility and shows a similar behavior as that of compressibility. On the basis of sound propagation in liquid, the increase in free length results in a decrease in the ultrasonic velocity. The similar behavior of inter molecular free length is suggested by Rastogi et al. [26] and Arul and Palaniappan [36].

According to a model proposed by Eyring and Kincaid [27], ultrasonic velocity decreases if the free length increases as a result of mixing components. Similar results are observed in all the mixtures studied. However, the increase in temperature, leads to the increase of free length due to thermal expansion of liquids.

Table 6
Values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) for pure liquids.

Liquids	$\beta \times 10^{10}$ Pa^{-1}			$L_f \times 10^{10}$ m			$V_f \times 10^7$ m^3 mol^{-1}			$\pi_i \times 10^{-6}$ Pa		
	Temperature (K)											
	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
Methyl benzoate	5.114	5.379	5.623	0.4513	0.4663	0.4814	1.4469	1.5221	1.693	381.284	380.786	372.735
Cyclohexane	8.592	8.935	9.317	0.5849	0.6012	0.6197	1.6577	1.9066	2.105	400.812	386.706	378.423
1-Propanol	8.770	9.027	9.354	0.5909	0.6043	0.6209	0.3358	0.4003	0.471	877.636	837.431	802.192
1-Butanol	8.209	8.474	8.710	0.5717	0.5855	0.5992	0.3095	0.3785	0.453	787.114	746.981	712.132
1-Pentanol	7.896	8.086	8.431	0.5607	0.5719	0.5895	0.2849	0.3459	0.414	721.807	684.944	654.566
1-Hexanol	7.433	7.647	7.904	0.5440	0.5562	0.5708	0.2578	0.2949	0.352	678.229	657.7390	627.5101

Table 7
Values of adiabatic compressibility (β), free length (L_f) and free volume (V_f) for system I.

Mole fraction		$\beta \times 10^{10}$ Pa^{-1}			$L_f \times 10^{10}$ m			$V_f \times 10^7$ m^3 mol^{-1}		
x_1	x_3	Temperature (K)								
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	6.3439	6.4785	6.7588	0.5025	0.5119	0.5278	2.248	2.4122	2.5234
0.4886	0.1204	6.5773	6.8213	7.1706	0.5117	0.5252	0.5436	1.9484	2.0662	2.1848
0.3691	0.2419	7.2437	7.5779	7.7736	0.537	0.5536	0.566	1.4544	1.5339	1.6510
0.3003	0.3457	7.5417	7.8406	7.9907	0.5479	0.5631	0.5738	1.3938	1.4665	1.5824
0.1829	0.4511	7.9598	8.2561	8.5642	0.5629	0.5778	0.5941	1.1482	1.2112	1.3271
0.0893	0.5519	8.6843	8.8963	9.445	0.5879	0.5998	0.6239	0.9539	1.0131	1.0694
0	0.6491	9.3023	9.7813	10.3727	0.6085	0.629	0.6538	0.7069	0.7623	0.8318

Table 8
Values of adiabatic compressibility (β), free length (L_f) and free volume (V_f) for system II.

Mole fraction		$\beta \times 10^{10}$ Pa^{-1}			$L_f \times 10^{10}$ m			$V_f \times 10^7$ m^3 mol^{-1}		
x_1	x_3	Temperature (K)								
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	6.3439	6.4785	6.7588	0.5025	0.5119	0.5278	2.248	2.4122	2.5234
0.4886	0.1204	5.9808	6.1987	6.4322	0.4879	0.5007	0.5148	2.2725	2.4614	2.6338
0.3691	0.2419	6.7944	7.3852	7.6311	0.52	0.5465	0.5608	1.8567	1.9791	2.1187
0.3003	0.3457	7.4666	8.2739	8.476	0.5451	0.5785	0.591	1.5976	1.6755	1.7728
0.1829	0.4511	8.1106	8.5523	8.8506	0.5682	0.5881	0.6039	1.3073	1.4105	1.4835
0.0893	0.5519	8.6976	8.9429	9.7171	0.5884	0.6014	0.6328	1.0424	1.1023	1.1701
0	0.6491	11.676	12.558	13.267	0.6818	0.7127	0.7394	0.6376	0.7031	0.7789

4.4. Free volume (V_f)

Free volume is one of the fundamental factors in explaining the variations in the physico-chemical properties of liquids and liquid mixtures. The free space and its dependent properties have close connection with molecular structure and it may show interesting features about interactions between like and unlike molecules.

Hirschfelder et al. [28] found that free volume of a solute molecule at a particular temperature and pressure depends only on the internal pressure of the liquid in which it is immersed. The weakening of molecular association leads to a large free volume available for molecular motion and the reverse effect gives rise to smaller free volume. From Tables 7–10, it is found that for all the mixtures, free volume decreases with increase in concentration of 1-propanol, 1-butanol, 1-pentanol and1-hexanol. It is also found that free volume increases with increase in temperature for all the systems. The decrease in free volume shows the increase in magnitude of interactions as reported by Ali and Nani [29] and Arul and Palaniappan [22]. This suggests the closed packing of molecules inside the shield.

In the Methyl benzoate structure there are a lot voids available for OH to penetrate and enter into the complexion, which provides information of hydrogen bonds between interacting components, pointed out by Trenzado et al. [25] and Casás et al. [30].

5. Excess parameters

In order to understand more about the nature of the interaction between the components of liquid mixture, it is necessary to discuss the same in terms of excess parameters rather than the actual values. The deviation of physical property of the liquid mixtures from the ideal behavior is the measure of the interaction between the molecules, which is attributed to either adhesive or cohesive forces (Hirschfelder et al. [28]). They can yield an idea about the non-linearity of the system as association or other type of interactions. According to Saleh et al. [31] the sign of excess molar values depends upon the relative magnitude of contractive and expansive effects which arises on mixing of liquid components.

The thermodynamic 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 parameters depend on the strength of interaction between unlike molecules. The dispersion forces are responsible for possessing positive excess values, while dipole-dipole, dipole-induced dipole, charge transfer interaction and hydrogen bonding between unlike molecules are responsible for possessing negative excess values of adiabatic compressibility, free length and internal pressure. Depending upon the nature of the liquids whether they are polar or non-polar, the signs and

Table 9
Values of adiabatic compressibility (β), free length (L_f) and free volume (V_f) for system III.

Mole fraction		$\beta \times 10^{10}$ Pa^{-1}			$L_f \times 10^{10}$ m			$V_f \times 10^7$ m^3 mol^{-1}		
x_1	x_3	Temperature (K)								
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	6.3439	6.4785	6.7588	0.5025	0.5119	0.5278	2.248	2.4122	2.5234
0.4886	0.1204	5.7922	6.1759	6.3371	0.4802	0.4998	0.511	1.7823	1.9866	2.0941
0.3691	0.2419	6.2475	6.6425	6.7635	0.4987	0.5183	0.5279	1.5676	1.7297	1.8970
0.3003	0.3457	6.7718	7.2642	7.6374	0.5192	0.542	0.561	1.3913	1.5354	1.6042
0.1829	0.4511	7.3662	7.7569	8.0086	0.5415	0.5601	0.5747	1.2319	1.2987	1.4246
0.0893	0.5519	8.0838	8.3411	8.7094	0.5673	0.5808	0.5991	0.9758	1.1227	1.1720
0	0.6491	8.5834	8.7473	8.8621	0.5845	0.5948	0.6043	0.6417	0.6872	0.7813

Table 10
Values of adiabatic compressibility (β), free length (L_f) and free volume (V_f) for system IV.

Mole fraction		$\beta \times 10^{10}$ Pa^{-1}			$L_f \times 10^{10}$ m			$V_f \times 10^7$ m^3 mol^{-1}		
x_1	x_3	Temperature (K)								
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	6.3439	6.4785	6.7588	0.5025	0.5119	0.5278	2.248	2.4122	2.5234
0.4886	0.1204	5.5648	5.9016	6.2312	0.4707	0.4886	0.5068	1.9998	2.1211	2.3104
0.3691	0.2419	6.0281	6.3904	6.5957	0.4899	0.5084	0.5214	1.7891	1.9008	2.0948
0.3003	0.3457	6.6965	7.2207	7.4305	0.5163	0.5404	0.5534	1.3077	1.4010	1.4962
0.1829	0.4511	7.0032	7.6165	7.7992	0.528	0.5505	0.5669	1.1940	1.2268	1.3022
0.0893	0.5519	7.723	8.0542	8.5168	0.5549	0.5708	0.5925	0.8133	0.8777	0.9513
0	0.6491	8.2899	8.9248	9.2765	0.5745	0.6008	0.6183	0.5405	0.6096	0.6325

Table 11
Values of excess adiabatic compressibility (β^E) and excess free length (L_f^E) for system I.

Mole fraction		$\beta^E \times 10^{10}$ Pa^{-1}			$L_f^E \times 10^{10}$ m		
x_1	x_3	Temperature (K)					
		303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	−0.1600	−0.3196	−0.3402	−0.0021	−0.0082	−0.0087
0.4886	0.1204	−0.3367	−0.5321	−0.3456	−0.0086	−0.0104	−0.0086
0.3691	0.2419	−0.3412	−0.3845	−0.4152	−0.0088	−0.0070	−0.0113
0.3003	0.3457	−0.1369	−0.2124	−0.3032	−0.0016	−0.0013	−0.0075
0.1829	0.4511	−0.0763	−0.1240	−0.0934	−0.0002	−0.0001	−0.0008
0.0893	0.5519	0.3055	0.2018	0.4389	−0.0117	−0.0091	−0.0160
0	0.6491	0.5948	0.7870	1.0323	−0.0198	−0.0258	−0.0338

magnitudes of these excess values can throw light on the strength of interactions.

5.1. Excess adiabatic compressibility (β^E)

From Tables 11, 13, 15 and 17 it is pointed out that the excess value of adiabatic compressibility are negative and tend to be positive with the increasing concentration of X_3 (alcohol) as well as rising of temperature in all systems studied. Sridevi et al. [19] found that the increasing negative value of excess compressibilites indicates a strong hetero-molecular interaction in the liquid mixtures, which is attributable to charge transfer, dipole-dipole, dipole-induced dipole interactions, and hydrogen bonding between unlike components. Positive values in excess properties correspond mainly to the existence of dispersive forces. The negative value of β^E is associated with a structure forming tendency while a positive value is taken to indicate a structure breaking tendency due to hetero molecular interaction between the component molecules of the mixtures. The negative β^E values for ternary mixtures indicate the formation of H bonds. The positive excess adiabatic compressibility which indicates loosely packed molecules in the mixtures results due to shape and size.

5.2. Excess free length (L_f^E)

On the close perusal of Tables 11, 13, 15 and 17, it is observed that the excess free length (L_f^E) values are negative for all the mixtures over the entire range of composition and the L_f^E values are observed to be positive at higher concentration.

According to Bai et al. [33], the negative values of excess intermolecular free length L_f^E indicate that sound waves cover longer distances due to decrease in intermolecular free length ascribing the dominant nature of hydrogen bond interaction between unlike molecules. Fort and Moore [34] indicated that the positive values of excess free length should be attributed to the dispersive forces and negative excess values are due to charge transfer, dipole-induced dipole and dipole-dipole interactions. In the present study the negative contribution of L_f^E in all systems shows the existence of strong interaction between the component of the mixtures and the positive contribution of L_f^E in all systems which shows the existence of dispersive forces between the components of the mixtures.

5.3. Excess free volume (V_f^E)

Tables 12,14,16 and 18 show that in all the systems the V_f^E values are positive and at higher concentration it tend to negative. This

Table 12
Values of excess free volume (V_f^E) and excess internal pressure (π_i^E) for system I.

Mole fraction		$V_f^E \times 10^7$ m^3 mol^{-1}			$\pi_i^E \times 10^{-6}$ Pa		
x_1	x_3	Temperature (K)					
		303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	0.7174	0.7369	0.6659	−49.012	−45.699	−38.133
0.4886	0.1204	0.5530	0.5290	0.4777	−80.389	−71.342	−61.473
0.3691	0.2419	0.3669	0.3216	0.2972	−138.920	−120.610	−106.930
0.3003	0.3457	0.2523	0.1886	0.1575	−118.900	−100.040	−87.634
0.1829	0.4511	0.1255	0.0546	0.0343	−124.050	−102.060	−88.229
0.0893	0.5519	0.0449	−0.0275	−0.0971	−124.440	−99.826	−81.495
0	0.6491	−0.0926	−0.1664	−0.2129	−93.544	−70.562	−54.644

Table 13
Values of excess adiabatic compressibility (β^E) and excess free length (L_f^E) for system II.

Mole fraction		$\beta^E \times 10^{10}$ Pa^{-1}			$L_f^E \times 10^{10}$ m		
x_1	x_3	Temperature (K)					
		303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	−0.1612	−0.3208	−0.3415	−0.0022	−0.0083	−0.0089
0.4886	0.1204	−0.8339	−1.0604	−0.9769	−0.0288	−0.0315	−0.0336
0.3691	0.2419	−0.3298	−0.1537	−0.0867	−0.0088	0.0025	0.0006
0.3003	0.3457	0.0329	0.4552	0.4495	0.0043	0.0225	0.019
0.1829	0.4511	0.3671	0.4536	0.5151	0.0153	0.0203	0.0201
0.0893	0.5519	0.6454	0.5653	1.0737	0.0236	0.0216	0.0373
0	0.6491	3.3140	3.9003	4.3147	0.1049	0.121	0.1321

Table 14
Values of excess free volume (V_f^E) and excess internal pressure (π_i^E) for system II.

Mole fraction		$V_f^E \times 10^7$ m^3 mol^{-1}			$\pi_i^E \times 10^{-6}$ Pa		
x_1	x_3	Temperature (K)					
		303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	0.7169	0.7365	0.6655	−49.124	−45.813	−38.245
0.4886	0.1204	0.8551	0.8999	0.8996	−92.150	−85.989	−78.049
0.3691	0.2419	0.553	0.5320	0.5084	−101.850	−90.329	−80.119
0.3003	0.3457	0.4076	0.3427	0.2847	−115.780	−98.438	−84.929
0.1829	0.4511	0.2312	0.1922	0.1212	−119.130	−101.730	−85.512
0.0893	0.5519	0.0801	−0.0016	−0.0682	−106.080	−81.909	−64.081
0	0.6491	−0.2111	−0.2866	−0.3357	−46.525	−27.827	−15.998

suggests that the component molecules are more close together in the liquid mixture than in pure liquids, indicating that strong attractive interactions, Parveen et al. [37]. Since Methyl benzoate is highly polar when compared to 1-alcohol, mixing of cyclohexane and alcohol with methyl benzoate ends to break dipolar association releasing several dipoles. Consequently, the free dipoles of Methyl benzoate would induce moments in the neighboring cyclohexane and alcohol molecules resulting in dipole-induced dipole interactions leading to contraction in volume. Another important factor is the large magnitude in excess values is the lower alcohol, corresponds to strong self-association of pure alcohol, which suggests the existence of strong interaction.

5.4. Excess internal pressure (π_i^E)

In Tables 12, 14, 16 and 18, it is found that the excess internal pressure values are negative and decreases with increasing mole fraction of X_3 (alcohol) as well as temperature in all the three systems studied. In the present investigation, the observed behavior of π_i^E shows the existence of specific interaction in all the systems studied, but the strength of interaction decreases with the rise of temperature resulting in the decrease of π_i^E values (Mariano and Postigo [35]).

6. Conclusions

Density, viscosity and ultrasonic velocity values were measured in ternary liquid mixtures for four systems with cyclohexane as common component, at three different temperatures.

i) A host of some of the acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure have been evaluated.
ii) The excess parameters of adiabatic compressibility, free length, free volume and internal pressure have been investigated.
iii) An analysis of the results suggests the presence of strong intermolecular interaction in all the ternary mixtures.
iv) The anomalous relationship observed in various excess parameters which attributed to the characteristic property that strong dipolar interactions and a highly directional interaction bonding act simultaneously between component molecules.
v) In the Methyl benzoate structure, there are a lot of voids available for OH to penetrate and enter into complexion, and also provides information regarding the presence of hydrogen bonds between interacting components.
vi) From the magnitude of velocity, the existence of molecular interactions in the mixture is in the order: 1-hexanol > 1-pentanol > 1-propanol > 1-butanol.

Table 15
Values of excess adiabatic compressibility (β^E) and excess free length (L_f^E) for system III.

Mole fraction		$\beta^E \times 10^{10}$ Pa^{-1}			$L_f^E \times 10^{10}$ m		
x_1	x_3	Temperature (K)					
		303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	−0.1612	−0.3208	−0.3415	−0.0022	−0.0083	−0.0089
0.4886	0.1204	−0.9912	−1.0446	−1.0442	−0.0354	−0.031	−0.0365
0.3691	0.2419	−0.8140	−0.8189	−0.8985	−0.0279	−0.023	−0.0304
0.3003	0.3457	−0.5678	−0.4382	−0.3053	−0.0183	−0.0099	−0.0081
0.1829	0.4511	−0.2518	−0.1867	−0.2152	−0.007	−0.0024	−0.0052
0.0893	0.5519	0.1878	0.1566	0.205	0.0079	0.0078	0.0084
0	0.6491	0.4058	0.3176	0.0725	0.0141	0.0111	0.0026

Table 16
Values of excess free volume (V_f^E) and excess internal pressure (π_i^E) for system III.

Mole fraction		$V_f^E \times 10^7$ m^3 mol^{-1}			$\pi_i^E \times 10^{-6}$ Pa		
x_1	x_3	Temperature (K)					
		303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	0.7169	0.7365	0.6655	−49.124	−45.813	−38.245
0.4886	0.1204	0.3672	0.4282	0.3637	−50.564	−48.862	−39.931
0.3691	0.2419	0.2688	0.2891	0.2946	−64.610	−59.408	−53.431
0.3003	0.3457	0.2088	0.2126	0.1299	−79.763	−70.503	−55.822
0.1829	0.4511	0.1658	0.0936	0.0783	−91.029	−73.540	−64.134
0.0893	0.5519	0.0256	0.0349	−0.0467	−85.415	−78.035	−59.001
0	0.6491	−0.1992	−0.2907	−0.318	−41.752	−19.110	−13.683

Table 17
Values of excess adiabatic compressibility (β^E) and excess free length (L_f^E) for system IV.

Mole fraction		$\beta^E \times 10^{10}$ Pa^{-1}			$L_f^E \times 10^{10}$ m		
x_1	x_3	Temperature (K)					
		303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	−0.1616	−0.3212	−0.3416	−0.0022	−0.0083	−0.0089
0.4886	0.1204	−1.1716	−1.2742	−1.0965	−0.0432	−0.0405	−0.0385
0.3691	0.2419	−0.9417	−0.9841	−0.9617	−0.0334	−0.0298	−0.0332
0.3003	0.3457	−0.5043	−0.35	−0.354	−0.0162	−0.0068	−0.0101
0.1829	0.4511	−0.4304	−0.1523	−0.2143	−0.0138	−0.0057	−0.0056
0.0893	0.5519	0.0585	0.0894	0.2763	0.0039	0.0057	0.0112
0	0.6491	0.3934	0.7626	0.8077	0.0142	0.0267	0.0280

Table 18
Values of excess free volume (V_f^E) and excess internal pressure (π_i^E) for system IV.

Mole fraction		$V_f^E \times 10^7$ m^3 mol^{-1}			$\pi_i^E \times 10^{-6}$ Pa		
x_1	x_3	Temperature (K)					
		303.15	308.15	313.15	303.15	308.15	313.15
0.5996	0	0.7174	0.7369	0.6659	−49.012	−45.699	−38.133
0.4886	0.1204	0.6138	0.5966	0.6176	−70.200	−63.643	−57.477
0.3691	0.2419	0.7313	0.7287	0.7864	−132.620	−122.970	−112.600
0.3003	0.3457	0.1932	0.1595	0.1124	−85.847	−77.015	−63.801
0.1829	0.4511	0.2065	0.1178	0.063	−91.712	−84.917	−69.868
0.0893	0.5519	−0.0526	−0.1047	−0.1496	−72.555	−61.700	−48.414
0	0.6491	−0.2084	−0.2507	−0.3351	−29.721	−16.374	−2.755

References

[1] Ali, A, Nain, AK & Abida 2004, 'Ultrasonic and volumetric study of molecular interactions in acetnitrile + 1-alkanols (C_6, C_8, C_{10}) binary mixtures at different temperatures', The Journal of Chinese Chemical Society, vol. 51, no.3, pp. 477–485.

[2] M.I. Arulaguppi, J.C. Barragi, Physico-chemical and excess properties of the mixtures of methylcyclohexane + ethanol + propan-1-ol + propan-2-ol + butan-1-ol + 2-methyl-1-propanol or 3-methyl-1-butanol at T = 298.15, 303.15 and 308.15 K, J. Chem. Thermodyn. 38 (4) (2006) 434–442.

[3] A.N. Kannappan, R. Palani, Ultrasonic investigations in amino acids with aqueous dimethyl formamide, Indian J. Chem., Sect. A 46 (2007) 54–59.

[4] T. Satyanarayan Rao, N. Veeraiah, C. Rambabu, Excess volume, viscosity and compressibility of the mixtures consisting of 0-cresol and m-cresol with N,N-dimethylacetamide at different temperatures, Indian J. Pure Appl. Phys. 40 (2002) 850–856.

[5] Rai, RD, Shukla, RK, Shukla, AK & Pandey, JD 1989, 'Ultrasonic speeds and isentropic compressibilities of ternary liquid mixtures at (298.15 ± 0.01) K', J. Chem. Thermodyn., vol. 21, no. 2, pp.125–129.

[6] P.S. Nikam, S.J. Kharat, Density and viscosity studies of binary mixtures of N, N-dimethylformamide with toluene and methyl benzoate at (298.15, 303.15, 308.15 & 313.15 K), J. Chem. Eng. Data 50 (2) (2005) 455–459.

[7] P.S. Nikam, V.M. Kapade, M. Hasan, Molecular interactions in binary mixtures of brombenzene with normal alkanols (C_1–C_4): an ultrasonic study, Indian J. Pure Appl. Phys. 38 (5) (2000) 170–173.

[8] Peralta, RD, Infante, R, Cortez, G & Wisniak, J 2004, 'Density, excess volumes, and partial volumes of the binary systems of dimethyl sulfoxide + ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene at 298.15 K, J. Solut. Chem., vol. 33, no.4, pp. 339–351.

[9] J.M. Resa, C. Gonzalez, J.M. Goenga, M. Iglesis, Influence of temperature n ultrasonic velocity measurements of ethanol + water + ethyl acetate mixtures, Phys. Chem. Liq. 43 (1) (2005) 65–89.

[10] K. Prasad, K. Siva Kumar, G. Prabhakar, P. Venkateswarlu, Molecular interactions in ternary organic liquid mixtures, J. Mol. Liq. 123 (2) (2006) 51–55.

[11] Nain, AK 2007, 'Ultrasonic and viscometric studies of molecular interactions in binary mixtures of tetrahydrofuran with some aromatic hydrocarbons at temperatures from 288.15 to 318.15 K, Phys. Chem. Liq., vol. 45, no. 4, pp. 371–388.

[12] S.L. Oswal, N.Y. Ghael, R.L. Gardas, Volumetric and transport properties of ternary mixtures containing 1-propanol + ethyl ethanoate + cyclohexane or benzene at 303.15 K: experimental data, correlation and prediction by ERAS model, Thermochim. Acta 484 (1) (2009) 11–21.

[13] H. Eyring, M.S. John, Significant Liquid Structures, Wiley, New York, 1969.

[14] D.R. Bhadja, Y.V. Patel, P.H. Paronia, Ultrasonic study of poly/R, R', 4, 4',-cyclohexylidene diphenylene phosphorochloride – DMF solutions at different temperatures, Indian J. Pure Appl. Phys. 24 (2) (2002) 47–53.

[15] Syamala, V, Kumar, KS & Venkateswarlu, P 2007, 'Volumetric behaviour of ternary organic liquid mixtures containing dimethylsulphoxide, 1, 2-dichlorobenzene and 1-alkanols at 303.15 K', J. Mol. Liq., vol. 136, no.1, pp. 29–34.

[16] L. Sarkar, M.N. Roy, Studies on liquid–liquid interactions of some ternary mixtures by density, viscosity, ultrasonic speed and refractive index measurements, Thermochim. Acta 496 (1) (2009) 124–128.

[17] J.M. Prausnitz, R.N. Lichtenthales, E.G. Azevedo, Molecular Thermodynamics of Fluid Phases Equilibria, Prentice Hall, New Jersey, 1986.

[18] M.J. Dávila, R. Alcalde, S. Aparicio, Compressed liquid density measurements for {methylbenzoate + (cyclohexane or 1-hexanol)} binary systems, J. Chem. Thermodyn. 43 (7) (2011) 1017–1022.

[19] U. Sridevi, K. Samatha, A.V. Sarma, Excess thermodynamic properties in binary liquids, Journal of Pure & Applied Ultrasonics 26 (4) (2004) 01–11.

[20] W. Kerboub, Z. Atik, A thermodynamic study on solubility and liquid–liquid phase behaviour for 2,2,2-trifluoroethanol + cyclohexane + 1-butanol at three temperatures and pressure 101.3 kPa, J. Chem. Thermodyn. 42 (11) (2010) 1330–1334.

[21] R. Thiyagarajan, L. Palaniappan, Molecular interaction study of two aliphatic alcohols with cyclohexane, Indian J. Pure Appl. Phys. 46 (12) (2008) 852–856.

[22] G. Arul, L. Palaniappan, Ultrasonic study of 1-butanol in pyridine with benzene, Indian J. Pure Appl. Phys. 43 (2005) 755–758.

[23] V. Kannappan, R.J. Shanthi, Ultrasonic study of induced dipole-dipole interactions in binary liquid mixtures, Indian J. Pure Appl. Phys. 43 (10) (2005) 750–754.

[24] M. Aravinthraj, S. Venkatesan, M. Kamaraj, Molecular interaction studies between H-bonded ternary mixtures of p-cresol with simple aldehydes in cyclohexane at different temperatures, Indian Journal of Chemical Environment and Pharmaceutical Research 2 (1) (2011) 5–11.

[25] J.L. Trenzado, J.S. Matos, R. Alcalde, Volumetric properties and viscosities of the methyl butanoateheptane + cyclooctane ternary system at 283.15 and 313.15 K and its binary constituents in the temperature range from 283.15 to 313.15 K, Fluid Phase Equilib. 200 (2) (2002) 295–315.

[26] M. Rastogi, A. Awasthi, M. Gupta, J.P. Shukla, Ultrasonic investigations of X… HO bond complexes, Indian J. Pure Appl. Phys. 40 (4) (2002) 256–263.

[27] H. Eyring, J.F. Kincaid, Free volumes and free angle ratio of molecules in liquids, The Journal of Chemical Physics 6 (10) (1938) 620–629.

[28] J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, Molecular Theory of Gases and Liquids, John Wiley and Sons, New York, 1954.

[29] A. Ali, A.K. Nani, Ultrasonic study of molecular interactions in binary liquid mixtures at 303.15 K, Journal of Pure and Applied Ultrasonics 21 (1999) 31–34.

[30] L.M. Casás, A. Touriño, B. Orge, G. Marino, M. Iglesias, J. Tojo, Thermophysical properties of acetone or methanol + n-alkane (C_9 to C_{12}) mixtures, J. Chem. Eng. Data 47 (4) (2002) 887–893.

[31] M.A. Saleh, S. Akhtar, M.S. Ahmed, M.H. Uddin, Excess molar volumes and thermal expansivities of aqueous solutions of dimethylsulfoxide, tetrahydrofuran and 1, 4-dioxane, Phys. Chem. Liq. 40 (5) (2002) 621–635.

[32] K. Ramamoorthy, S. Alwan, Calculation of free volume from ultrasonic velocity, J. Curr. Sci. 47 (10) (1978) 334–339.

[33] M.E. Bai, M.C.S. Subha, G.N. Swamy, K.C. Rao, Acoustical studies of molecular interactions in binary liquid mixtures of butoxy ethanol with some amines at 308.15 K, Journal of Pure and Applied Ultrasonics 26 (2) (2004) 79–83.

[34] R.J. Fort, W.R. Moore, Viscosities of binary liquid mixtures, Trans. Faraday Soc. 62 (1966) 1112.

[35] A. Mariano, M. Postigo, Excess molar volume and viscosity study for the ternary system tetrahydrofuran (1) + 1-chlorobutane (2) + 2-butanol (3) at 283.15, 298.15 and 313.15 K, Fluid Phase Equilib. 239 (2) (2006) 146–155.

[36] G. Arul, L. Palaniappan, Molecular interaction studies in the ternary mixtures of cyclohexane + toluene+2-Propanol, Indian J. Pure Appl. Phys. 39 (9) (2001) 561–564.

[37] S. Parveen, S. Divya, S. Singh, K.P. Singh, M. Gupta, J.P. Shukla, Ultrasonic velocity, density, viscosity and their excess parameters of the binary mixtures of tetrahydrofuran with methanol and o-cresol at varying temperatures, Appl. Acoust 70 (3) (2009) 507–513.