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Prediction of Speeds of Sound in the Binary Mixtures of Ethyl Lactate with Cyclohexanone, Cyclohexylamine and Cyclohexanol at 303.15 K

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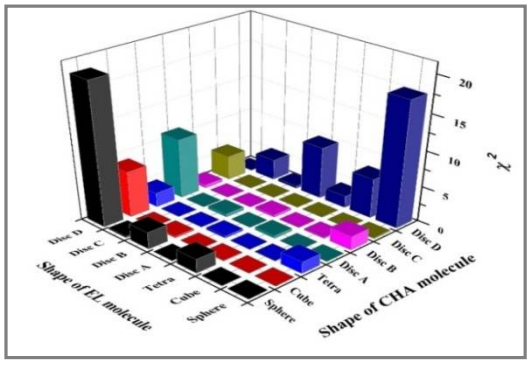
ABSTRACT

Densities and speeds of sound of binary mixtures of ethyl lactate with cyclohexanone, cyclohexylamine and cyclohexanol including those of pure liquids are measured over the entire composition range at temperature 303.15 K. A comparative study of experimentally measured and theoretically predicted speeds of sound at 303.15 K is made using different theories viz., Nomoto, impedance, Van Gael and Vangeel, Junjie, Rao and collision factor theories. Scaled particle and free length theories are applied to these mixtures by considering different shapes viz., sphere, cube, tetrahedron, disc A, disc B, disc C and disc D for both the participating components i.e., ethyl lactate with cyclohexanone, cyclohexylamine and cyclohexanol. From the experimental data, various thermodynamic parameters viz., molar volume, intermolecular free length and isentropic compressibility useful in the computation of theoretical speeds of sound in the mixtures are calculated. Chi-square test is applied for the goodness of the fit to investigate the relative applicability of these theories to the binary liquid mixtures under investigation by considering 196 combinations of different molecular shapes and thermodynamic states at 303.15 K and a close agreement is found between theoretically predicted speeds of sound and the experimental values.

Graphical Abstract



χ^2 values corresponding to different shape combinations
of ethyl lactate and cyclohexylamine molecules using scaled particle theory

Highlights

- Binary liquid mixtures of ethyl lactate + cyclohexanone, cyclohexylamine and +cyclohexanol are investigated
- Correlation between experimental and theoretical speeds of sound is made
- Shapes and thermodynamic states of the molecules are considered in scaled particle and free length theories
- Scaled particle theory accurately predicted the speeds of sound in the mixtures studied
- Statistical analysis is made by determining standard deviation and by applying Chi-square test

Keywords: Ultrasonics, Thermodynamic parameters, Scaled particle theory, *Chi*-square.

INTRODUCTION

Speed of sound studies are used successfully in a wide range of applications in materials science, medicine, metallurgy, cleaning, nondestructive testing, under water sound, welding of plastics and metals, atomization of liquids, chemical effects and cell disruption [**1**]. In many chemical reactions, liquid solvents are very significant and the choice of a proper solvent for a process mainly depends on the availability of its physical properties like nontoxicity, relatively nonhazardous and noncorrosive nature. Ethyl lactate is an important solvent because of its distinctive features like high solvency power, 100% biodegradability and environmental friendly nature [**2**]. Cyclic ketones like cyclo-hexanone are miscible with organic solvents and acts as a good solvent for paints, cellulose ethers, etc. [**3**]. Cyclohexylamine is significant because of its miscibility with polar and nonpolar substances and has wide applications in the production processes of insecticides, emulsifying agents, dyes, dry cleaning agents and corrosion inhibitors [**4**]. Cyclohexanol is used as an intermediary substance in the production of nylon and other plastic materials, as a solvent in paint and textile industries [**5**].

The measurement of speed of sound enables accurate determination of the coefficients of isentropic compressibility which can be used to provide qualitative information about the physical nature of the aggregates occurring in the liquid phase. The study of molecular interaction between the components of binary liquid mixtures, using speeds of sound and thermodynamic parameters derived from it, has been the subject matter of several earlier workers [**6-8**]. As the speed of sound in liquid mixtures is known to be a quantity which depends on concentration in a variety of manners according to the nature of each component liquid, it is of considerable interest and importance to establish a formula to predict the speed of sound in liquid mixtures. This, however, is not an easy task as the concentration dependency of speed of sound in the liquid mixtures does not show a standard pattern like linear/nonlinear variations and in some cases even exhibiting maximum or minimum at certain concentrations. Several researchers [**9-11**] carried out ultrasonic investigations on liquid mixtures and correlated the experimental results of speed of sound with the theoretical relations of Nomoto, Van Dael and Vangeel, impedance relation, Rao's specific speed of sound, Junjie's relation, Jacobson's free length theory (FLT) and Schaff's collision factor theory (CFT) and interpreted the results in terms of molecular interactions.

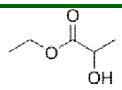
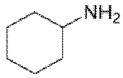
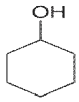
The objective of the present work is to compare the merits of the theoretically calculated speeds of sound in the binary liquid mixtures of ethyl lactate with cyclohexanone, cyclohexylamine and cyclohexanol at a temperature 303.15 K over the entire composition range using different theories *viz*., Nomoto, impedance, Van Gael and Vangeel, Junjie, Rao, collision factor, free length and scaled particle theories with the experimentally measured values. An attempt is made to study the change in the shapes and thermostatic states of the interacting molecules using scaled particle and free length theories.

MATERIALS AND METHODS

A single pan electronic balance (Shimadzu AY120) with an uncertainty of ±0.01 milligram is used for the preparation of various compositions of the liquid mixtures with an uncertainty of 1×10^{-4} in the mole fraction and the prepared mixtures are stored in air-tight glass bottles. The liquids are thoroughly mixed before being transferred into the apparatus used for the determination of the speed of sound and density. The required properties are measured within one day of the preparation of the mixture. Speed of sound measurements are made with the help of single crystal ultrasonic pulse echo interferometer developed using the concept of Mc.Skimin [**12**]. Number of pulses satisfying in phase condition is counted and the separation between them is estimated in terms of the pulse repetition rate.

The speeds of sound in the liquid mixtures are measured by single crystal variable path fixed frequency interferometer, Model-F 05 supplied by Mittal Enterprises, New Delhi at a fixed frequency of 2 MHz with an uncertainty less than 0.1%. Temperature of the mixture is kept constant at 303.15 K for the measurement of speeds of sound using a microprocessor assisted circulating water bath, (supplied by Mac, New Delhi) regulated to ±0.01 K. The densities of the mixtures are measured using a vibrating-tube Rudolph Research Analytical density meter, model DDM-2911 automatically thermostated within ± 0.01 K. The uncertainty in density measurements is ± $1x10^{-5}$ g·cm^{-3}. The details of chemicals used in this work, their purity, structure and purification etc. are given in table 1.

Table 1. Details of chemicals used with CAS number, source, purification method, structure and molar mass

Chemical	CAS number	Supplier	Purification technique (Purity% GC)	Chemical structure	Molar mass 10^{-3} kg mol^{-1}
Ethyl lactate	97-64-3	Merck	Vacuum distillation (99.7)		118.13
Cyclohexanone	108-94-1	S.D Fine	Fractional distillation (99.6)		98.14
Cyclohexylmine	108-91-8.	S.D Fine	Fractional distillation (99.3)		99.17
Cyclohexanol	108–93–0	S.D Fine	Fractional distillation (99.5)		100.16

RESULTS AND DISCUSSION

From the ultrasonic point of view, the speed of sound, density, molar volume, isentropic compressibility, free length etc., are found to be strongly affected by the changes of composition besides the type of bonding present between the molecules of the constituent liquids. The experimental speeds of sound and densities of the pure liquids i.e., ethyl lactate, cyclohexanone, cyclohexylamine and cyclohexanol at 303.15 K are presented in table 2 along with the literature values. Comparison of the experimental and literature values of speed of sound and density confirm the purity of the chemicals used in the present investigation.

The experimental speed of sound (U) and density (ρ) of the binary mixtures of ethyl lactate with cyclohexanone, cyclohexylamine and cyclohexanol at temperature 303.15 K over the entire composition are listed in table 3. Variations of speed of sound and density with the mole fraction of ethyl lactate for all the systems are presented respectively in figures 1 and 2. For the smooth representation, the values of speeds of sound and density of the binary mixtures are fitted to suitable polynomial equations.

Table 2. Comparison of the experimental speeds of sound (U/ms^{-1}) and density (ρ/kgm^{-3}) of ethyl lactate, cyclohexanone, cyclohexylamine and cyclohexanol with the literature data at 303.15 K

Compound	U/ms^{-1}		ρ/kgm^{-3}	
	Exp.	Lit.	Exp.	Lit.
Ethyl lactate	1261.14	1261.17[a]	1022.74	1022.81[b]
Cyclohexanone	1388.34	1388.3[c]	937.35	937.24[d]
Cyclohexylamine	1397.74	1397.8[e]	857.64	857.671[f]
Cyclohexanol	1443.13	1443.2[e]	941.43	941.32[e]

Ref. a[24], b[25], c[26], d[27], e[28], f[29]

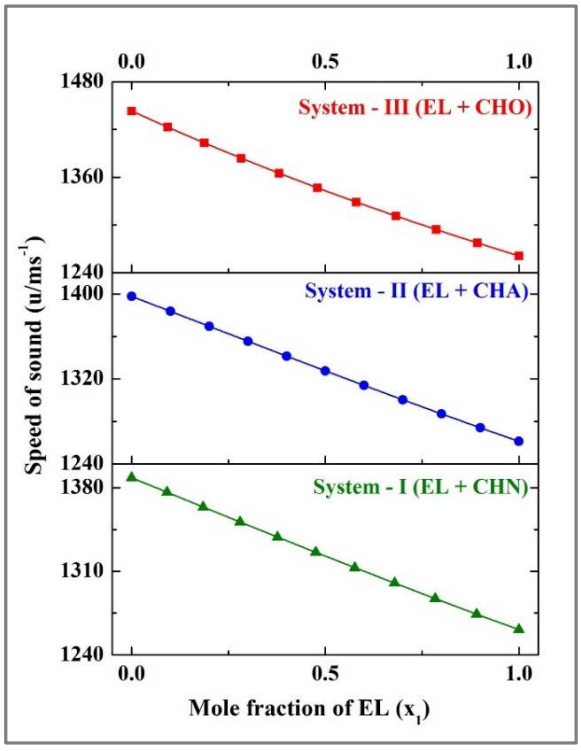


Figure 1. Variation of speed of sound (U/ms^{-1}) of pure liquids with the mole fraction of ethyl lactate

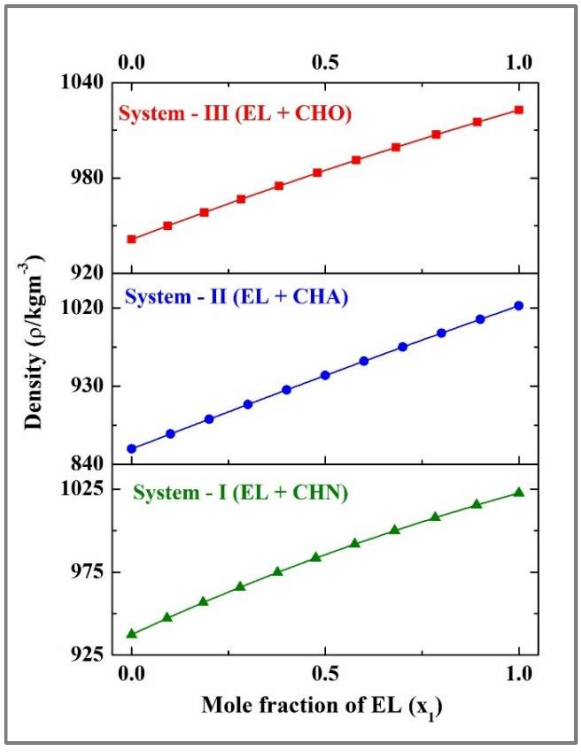


Figure 2. Variation of density (ρ/kgm^{-3}) of pure liquids with the mole fraction of ethyl lactate

From the fitted experimental data of speed of sound and density of liquid mixtures, various acoustic and thermodynamic parameters viz., molar volume (V_m), isentropic compressibility (κ_s), intermolecular free length (L_f) useful for the theoretical prediction of the speed of sound in the theories proposed by various researchers are computed using the equations:

$$\text{Molar volume}, V_m = \overline{M}/\rho \qquad (1)$$

$$\text{Isentropic compressibility}, \kappa_s = \rho^{-1}U^{-1} \qquad (2)$$

$$\text{Intermolecular free length}, L_f = K(\kappa_s)^{1/2} \qquad (3)$$

where $\overline{M}$ is the average molecular weight of the mixture and K is temperature dependent constant

From figure 1, it can be concluded that the speed of sound decreases nonlinearly with the increase of mole fraction of ethyl lactate at 303.15 K indicating intermolecular interactions between the components of the liquid mixtures. The variation of speed of sound in a solution depends upon the

increase or decrease of intermolecular free length after mixing the components. According to Eyring and Kincaid [13], speed of sound should decrease if the intermolecular free length increases as a result of mixing of components as is observed in the present investigation (table 3). From figure 2, it is noticed that the density for all the three liquid mixtures increases with the increase in concentration of ethyl lactate probably due to solvent-solvent interactions in the corresponding liquid mixtures.

Theories of speed of sound: In the present work, the speed of sound in three binary liquid mixtures under investigation viz., ethyl lactate +cyclohexanone, +cyclohexylamine and +cyclohexanol is evaluated using semi-empirical formulations of Nomoto, impedance relation, Van Dael and Vangeel, Rao, Junjie, Schaaff's, modified Jacobson's free length theory and scaled particle theory and compared the relative merits of these theories. The applicability of the theoretical models is also checked by computing the standard deviation in speed of sound, Σdu and by Chi-square fit (χ^2), which enables to find whether the deviations of the theoretical values from the experimental ones are due to chance or really due to the inadequacy of the theory to fit the data. The extent of deviation in various theories may be attributed to the presumptions made in the theories for the consideration of nonpolar-polar and polar-polar interaction between the molecules. Molecules constantly remain under the effect of active collisions. Such an evaluation offers a simple method to investigate molecular interactions in addition to verifying the applicability of those theories to liquid mixtures.

Table 3. Experimental speeds of sound (U/m s^{-1}), densities (ρ/kg m^{-3}), and computed molar volumes ($V_m/10^{-6}$ m^3 mol^{-1}), isentropic compressibilities ($\kappa_s/10^{-10}$ m^2 N^{-1}) and mean free lengths ($L_f/10^{-11}$ m) for the binary mixtures of ethyl lactate + cyclohexanone, + cyclohexylamine and + cyclohexanol at a temperature 303.15 K

x_1	U	ρ	V_m	κ_s	L_f	x_1	U	ρ	V_m	κ_s	L_f
Ethyl lactate (1) + Cyclohexanone (2)											
0.0000	1388.34	937.35	104.70	5.5349	4.8830	0.5762	1313.06	991.86	110.56	5.8477	5.0191
0.0915	1376.19	947.17	105.55	5.5746	4.9005	0.6790	1300.14	999.96	111.72	5.9162	5.0484
0.1848	1363.85	956.68	106.44	5.6195	4.9202	0.7838	1287.16	1007.81	112.93	5.9890	5.0794
0.2798	1351.33	965.90	107.39	5.6694	4.9420	0.8908	1274.16	1015.40	114.19	6.0662	5.1120
0.3767	1338.68	974.83	108.40	5.7242	4.9659	1.0000	1261.14	1022.74	115.50	6.1476	5.1462
0.4755	1325.91	983.48	109.45	5.7837	4.9916						
Ethyl lactate (1) + Cyclohexylamine (2)											
0.0000	1397.74	857.64	115.63	5.9682	5.0706	0.6003	1313.89	958.82	115.30	5.0191	5.1016
0.1001	1383.69	874.85	115.53	5.9702	5.0714	0.7002	1300.36	975.10	115.32	5.0484	5.1115
0.2002	1369.58	891.94	115.44	5.9771	5.0743	0.8002	1287.06	991.19	115.36	5.0794	5.1222
0.3002	1355.49	908.90	115.37	5.9881	5.0790	0.9001	1273.98	1007.07	115.42	5.1120	5.1338
0.4003	1341.48	925.71	115.33	6.0029	5.0853	1.0000	1261.14	1022.74	115.50	5.1462	5.1462
0.5003	1327.60	942.35	115.30	6.0208	5.0929						
Ethyl lactate (1) + Cyclohexanol (2)											
0.0000	1443.13	941.43	106.39	5.1004	4.6874	0.5801	1328.72	991.25	111.56	5.7141	4.9615
0.0928	1422.85	949.90	107.20	5.2000	4.7330	0.6825	1311.22	999.27	112.51	5.8206	5.0075
0.1872	1403.08	958.32	108.03	5.3006	4.7786	0.7865	1294.14	1007.19	113.48	5.9283	5.0536
0.2830	1383.80	966.67	108.87	5.4023	4.8242	0.8924	1277.45	1015.01	114.48	6.0373	5.0998
0.3805	1364.99	974.95	109.75	5.5050	4.8698	1.0000	1261.14	1022.74	115.50	6.1476	5.1462
0.4795	1346.63	983.15	110.64	5.6090	4.9156						

Nomoto theory: Nomoto [14] derived an empirical formula for the speed of sound in binary liquid mixtures consisting of two component liquids by assuming the additively of molar sound speed (R) without any change in volume on mixing:

$$U_{Nom} = \left[\frac{(x_1R_1 + x_2R_2)}{(x_1V_1 + x_2V_2)}\right]^3 \qquad (4)$$

where molar sound speed $R = \left(\frac{M}{\rho}\right)U^{\frac{1}{3}} = V_m U^{\frac{1}{3}}$.

Impedance relation: Using the impedance relation [15], the sound speed in the mixture is computed from the knowledge of speed of sound and density of pure components from the expression:

$$U = \frac{\sum x_i \rho_i U_i}{\sum x_i \rho_i} \qquad (5)$$

Van Dael and Vangeel relation: The ideal mixing theory of Van Dael and Vangeel [16] yield the relation for speed of sound in liquid mixtures as:

$$\frac{1}{(x_1 M_1 + x_2 M_2) U_{VDV}^2} = \left(\frac{x_1}{M_1 U_1^2} + \frac{x_2}{M_2 U_2^2}\right) \qquad (6)$$

where U_{VDV} is the ideal mixing speed of sound in the liquid mixture, $U_1$and U_2 are speeds of sound in pure liquidsand M_1 and M_2 are the molecular weights of the pure liquids.

Junjie relation: Junjie [17] assumed that the speed of sound in the mixture depends on the mole fraction, molecular weight and density of the mixture as:

$$U_{Jun} = \left[\frac{\left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right)}{(x_1 M_1 + x_2 M_2)^{0.5}\left(\frac{x_1 M_1}{\rho_1^2 U_1^2} + \frac{x_2 M_2}{\rho_2^2 U_2^2}\right)^{0.5}}\right] \qquad (7)$$

Rao's specific speed of sound formula: Using the ratio of the temperature coefficient of speed of sound and expansion coefficient, Rao [18] derived a formula for speed of sound given by:

$$U_{Rao} = (\sum x_i r_i \rho)^3 \qquad (8)$$

where r_i is the Rao's specific speed of sound and is given by $r_i = U_i^{1/3}\rho_i$.

Schaaffs' collision factor theory: Schaaffs [19] deduced a relation between the speed of sound in the liquid mixture and van der Waal's constant considering the speed of sound in ideal liquids to be a linear function of the weight percentages of the mixtures. Based on Schaaffs' collision factor theory, the speeds of sound of the binary mixture are calculated using the expression:

$$U_{CFT} = U_\infty (x_1 S_1 + x_2 S_2)(x_1 B_1 + x_2 B_2)/V_m \qquad (9)$$

where U_∞=1600ms^{-1}; S_1 and S_2 are the collision factors and B_1 and B_2 are the actual volumes of the component molecules 1 and 2 per mole respectively.

B_i and S_i are evaluated using the following equations:

$$B_i = \frac{4}{3}\pi r^3 N_A \quad \text{and} \quad S_i = \frac{U_i}{U_\infty}\frac{V_i}{B_i}$$

where r is the molecular radius of pure component, N_A is the Avogadro's number and V_i is the molar volume of i^{th} component.

Molecular radius in terms of the van der Waal's constant b is calculated using:

$$r = \left(\frac{3b}{16\pi N_A}\right)^{1/3} \text{and van der Waal's constant } b = V_m\left[1 - \frac{RT}{MU^2}\left\{\left(1 + \frac{MU^2}{3RT}\right)^{0.5} - 1\right\}\right]$$

However, the common drawback of the above theoretical models is that, the shapes and thermodynamic states of the participating molecules have not been taken into consideration. For the theoretical prediction of speeds of sound in liquid mixtures, free length theory was developed by considering the shapes and thermodynamic states of the component molecules and scaled particle theory was developed taking into account the shapes of the molecules.

Free length theory (FLT): Using the simplest property of the liquids viz., intermolecular free length L_f Jacobson [**20**] derived a relationship between the speed of sound in liquid mixture and the intermolecular free length. When compared with the above mentioned theories, in most of the liquid mixtures studied by various researchers Jacobson's original free length theory results in more deviation of evaluated speeds from the experimental values. Kalidoss [**21**] incorporated both the shape factor and thermostatic state into free length theory and found a close agreement between theoretical and experimental results. The modified free length is applied to the liquid mixtures under investigation viz., ethyl lactate + cyclohexanone, + cyclohexylamine and + cyclohexanol.

In terms of the shape parameters a and b, the volume and surface area of a liquid molecule are:

$$V = ar^3 \text{ and } S = br^2 \qquad (10)$$

Then, in one mole of a pure liquid, the surface area of all the molecules can be written as:

$$Y = Nbr^2 = F(36\pi N_A V_0^2)^{1/3}$$

$$\text{where } F = \frac{b}{(36\pi a^2)^{\frac{1}{3}}} \qquad (11)$$

where, N_A is the Avogadro's number, F is the shape factor giving the relation between the surface of the molecules and the imagined spherical surface which enclosed the same volume as the volume of the molecules. The different shapes considered in this work are given in table 4.

Jacobson considered only spherical shapes and monomeric state of the molecules and hence the values of the shape factor F and the association factor A are taken as unity.

V_0 is the volume of pure liquid at 0 K and is given by:

$$V_0 = V_T \left[1 - \left(\frac{T}{T_c}\right)\right]^{0.3} \qquad (12)$$

where T_c is the critical temperature and V_T is the molar volume at T K.

If A_i is the association factor and F_i is the shape factor of the i^{th} liquid molecule, according to Kalidoss, the expression for the intermolecular free length for the binary mixture becomes:

$$L_f = \frac{2\left[\left(\frac{\Sigma x_i A_i M_i}{\rho}\right) - \Sigma x_i A_i V_{0i}\right]}{\Sigma x_i A_i F_i Y_i} \qquad (13)$$

where x_i and M_i are the mole fraction and the molecular weight respectively of the i^{th} liquid. A_i =1 and 2 refer to the monomeric and dimeric states of the molecules. The above equation reduces to that originally proposed by Jacobson, with A_i=1 and F_i =1.

The speed of sound in the binary liquid mixture is calculated from this value of L_f and density of the mixture, using the relation:

$$U_{FLT} = \frac{K}{L_{f_{mix}} \rho_{exp}^{1/2}} \qquad (14)$$

where K is the Jacobson's temperature dependent constant.

Using the literature value of T_c, experimental density, mole fraction and shape factor by considering various shapes and the two possible thermostatic states of both the liquid molecules as input data, the intermolecular free length L_f and the speed of sound in the binary liquid mixture, U_{FLT} is calculated. In the present investigation, seven shapes viz., sphere, cube, tetrahedron, disc A, disc B, disc C and disc D of the individual components and two thermodynamic states viz., monomer and dimer are considered. For a given mixture 7 x 2 x 7 x 2 =196 combinations of F_i and A_i values were considered for the theoretical prediction of speeds of sound in the binary liquid mixtures of ethyl lactate +cyclohexanone, +cyclohexylamine and +cyclohexanol. The set of F_i and A_i values which generates the minimum χ^2 gives the corresponding shape and thermostatic state of the component liquid molecules in mixture.

Scaled particle theory (SPT): In pure state, generally the shapes of the molecules of a liquid are assumed to be spherical. However, when two liquids are mixed, the interaction between the component molecules affects the shapes of the participating liquid molecules. Like free length theory, in scaled particle theory also [**22, 23**] 7 shapes *viz.*, sphere, cube, tetrahedron, disc A, disc B, disc C and disc D of the participating components are considered and when the participating components have the correct shapes the theoretical speed of sound estimated based on this model will give values close to the experimental values. Scaled particle theory links the microscopic parameters *viz.*, radius, surface area and hard core volume of a molecule with the macroscopic parameters like speed of sound.

According to the scaled particle theory, the equation of state of a fluid is

$$\frac{p}{\rho_N K_B T} \frac{1+\eta+\eta^2}{(1-\eta)^2} \qquad (15)$$

where ρ_N is the number density, $\eta = V_H \rho_N$, V_H being hard core volume of the molecule and other quantities have usual meaning.

Scaled particle theory for mixtures of hard convex molecules gives the equation for the mixture as follows:

$$\frac{p}{\rho_N K_B T} = \frac{1}{(1-V\rho_N)^2} + \frac{AB\rho_N}{(1-V\rho_N)^2} + \frac{B^2 C \rho_N^2}{3(1-V\rho_N)^3} \qquad (16)$$

where $A = \Sigma x_i R_i$, $B = \Sigma x_i S_i$, $C = \Sigma x_i R_i^2$, $V = \Sigma x_i V_H$

R_i, S_i and V_{Hi} are the mean radius of curvature, surface area and volume respectively of a molecule of species i, ρ_N is the number density of the mixture molecule, x_i is the mole fraction.

Relating this with the equation

$$\gamma \left(\frac{dp}{d\rho}\right)_T = U^2, \text{ we get}$$

$$\frac{MU^2}{\gamma RT} = \frac{1}{(1-V\rho_N)^2} + \frac{2AB\rho_N}{(1-V\rho_N)^2} + \frac{B^2 C \rho_N^2}{3(1-V\rho_N)^2} \qquad (17)$$

For pure liquids, the above equation becomes

$$\frac{MU^2}{\gamma RT} = \frac{(1+(X-1)\eta)^2}{(1-\eta)^2} \qquad (18)$$

where X = RS/V is called the shape parameter.

The mean radius of the molecule is R = Y $(V_H)^{1/3}$and the surface area of the molecule is S = Z R^2, where Y and Z are the parameters related to the shape of the liquid molecule. The characteristic parameters used in the computational aspects of scaled particle theory are summarized in table 4 and table 5.

Table 4. Molecular assignment for different shapes

Shape	Size	R	S	V_H
Sphere	Radius=a	a	$4\pi a^2$	$4\pi a^3/3$
Cube	Side = *l*	3/4	$6l^2$	l^3
Tetrahedron	Side = *l*	$(3/\arctan\sqrt{2})/2\pi$	$\sqrt{3}l^2$	$(\sqrt{2}/12)l^3$
Discs		Radius=a and depth=*l*		
Disc A	*l* = a	$(\pi+1)a/4$	$4\pi a^2$	πa^3
Disc B	*l* = a/4	$(\pi+0.25)a/4$	$5\pi a^2/2$	$\pi a^3/4$
Disc C	*l* = a/2	$(\pi+0.50)a/4$	$3\pi a^2$	$\pi a^3/2$
Disc D	*l* = a/10	$(\pi+0.10)a/4$	$11\pi a^2/5$	$\pi a^3/10$

Table 5. Shape parameters

Shape	X	Y	Z
Sphere	3.0000	0.6204	12.5664
Cube	4.5000	0.7500	10.6666
Tetrahedron	6.7035	0.9303	8.3247
Disc A	4.1416	0.7070	11.7218
Disc B	8.4790	0.9190	10.9244
Disc C	5.4624	0.7832	11.3712
Disc D	17.8274	1.1920	10.5253

Among 196 (7 x 2 x 7 x 2) sets of the shapes (7) and thermodynamic states (2) assumed in free length theory, the set of shape-state of liquid 1 with shape-state of liquid 2 which yielded minimum χ^2 values are also presented in table 6. Along with the shapes and thermodynamic states of the interacting molecules for all the three binary liquid mixtures under investigation. Similarly, out of 49 (7 x 7) combinations of the shapes of the associating molecules considered in scaled particle theory, the combination of the shapes of the molecules which gave minimum χ^2 values are presented in table 6.

Table 6. Minimum values of χ^2 and corresponding shapes and thermodynamic states of the molecules obtained using SPT and FLT for the binary mixtures of ethyl lactate +cyclohexanone, +cyclohexylamine and +cyclohexanol at 303.15 K

Mixture	Theory	ΣdU	χ^2	Shape	
				Molecule 1	Molecule 2
Ethyl lactate (1) + cyclohexanone (2)	SPT	0.0019	0.0007	Disc C	Cu
	FLT	0.031	0.281	Disc C (Dimer)	Sp (Monomer)
Ethyl lactate (1) + cyclohexylamine (2)	SPT	0.0015	0.0004	Disc C	Disc A
	FLT	0.058	0.551	Te (Monomer)	Disc A (Monomer)
Ethyl lactate (1) + cyclohexanol (2)	SPT	0.0042	0.0029	Disc C	Disc A
	FLT	0.038	0.240	Te (Monomer)	Disc A (Monomer)

The corresponding shapes of the molecules of the three liquid mixtures are also presented in table 6. From the obtained χ^2 values, it is clear that even after taking into account the shapes and thermodynamic states of the molecules, the modified FLT failed to predict the speeds of sound in the binary liquid mixtures under investigation when compared with those predicted from SPT.

From table 6, it is clear that at 303.15 K, the speeds of sound computed from free length theory agree well with the experimental values when the shapes and states of molecules of (a) EL+CHN binary mixture are disc C-dimer (EL)+sphere-monomer (CHN), (b) EL+CHA binary mixture are tetrahedron-monomer (EL)+disc A-monomer (CHA) and (c) EL+CHO binary mixture are tetrahedron-monomer (EL)+ disc A-monomer (CHO). Also, the speeds of sound estimated from scaled particle theory are found to be very close to the experimental values when (a) the molecules of EL+CHN binary mixture takes the shapes of disc C (EL)+cube (CHN), (b)the molecules of EL+CHA binary mixture takes the shapes of disc C (EL)+disc A (CHA) and (c) the molecules of EL+CHO binary mixture takes the shapes of disc C (EL)+disc A (CHO).

The values of standard deviation Σdu and χ^2 obtained in the theoretical estimation of speed of sound using formulations of Nomoto, impedance relation, Van Dael and Vangeel, Rao, Junjie and Schaaff's, and the minimum values of Σdu and χ^2 obtained from free length and scaled particle theories are presented in table 7. Comparison of χ^2 values obtained from various theories of speed of sound for the binary mixtures of ethyl lactate (EL) +cyclohexanone (CHN), +cyclohexylamine (CHA) and +cyclohexanol (CHO) at 303.15 K are represented in figure 3. From table 7 and figure 3, it is clear that there is a close agreement between the experimental speeds of sound and those calculated using all the theoretical models for all the three binary mixtures at 303.15 K. However, from the chi-square test, it is observed that the χ^2 values are minimum for the speeds of sound computed using scaled particle theory for all the three binary liquid mixtures under investigation.

Table 7. Values of standard deviation ΣdU and χ^2 obtained using theoretical models for the binary mixtures of ethyl lactate + cyclohexanone, + cyclohexylamine and + cyclohexanol at 303.15 K

System	U_{NOM}	U_{IMP}	U_{VDV}	U_{JUN}	U_{RAO}	U_{CFT}	U_{FLT}	U_{SPT}
Ethyl lactate (1) + Cyclohexanone (2)								
ΣdU	0.011	0.004	0.012	0.021	0.005	0.010	0.031	0.0019
χ^2	0.020	0.003	0.024	0.073	0.004	0.015	0.028	0.0007
Ethyl lactate (1) + Cyclohexylamine (2)								
ΣdU	0.003	0.021	0.013	0.013	0.003	0.009	0.058	0.0015
χ^2	0.002	0.073	0.028	0.028	0.002	0.013	0.055	0.0004
Ethyl lactate (1) + Cyclohexanone (2)								
ΣdU	0.017	0.027	0.014	0.005	0.035	0.044	0.038	0.0042
χ^2	0.047	0.119	0.035	0.005	0.205	0.326	0.024	0.0029

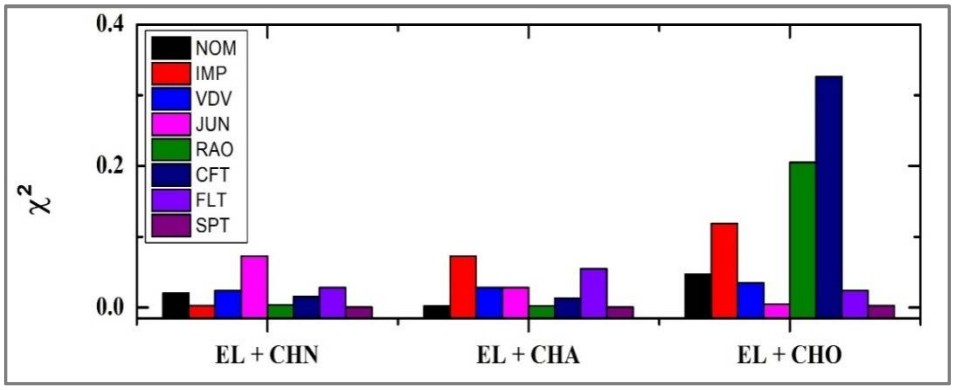


Figure 3. Comparison of various theories of speed of sound for the binary mixtures of ethyl lactate (EL) + cyclohexanone (CHN), + cyclohexylamine (CHA) and + cyclohexanol (CHO) at 303.15 K.

The speeds of sound calculated using different theories in the binary liquid mixtures under investigation viz., ethyl lactate + cyclohexanone, + cyclohexylamine and + cyclohexanol at 303.15 K are presented in table 8 along with the corresponding experimental speeds of sound.

Table 8. Theoretical speeds of sound (U/ms^{-1}) calculated by various theories along with experimental speeds of sound in the binary mixtures of ethyl lactate + cyclohexanone, + cyclohexylamine and + cyclohexanol at 303.15 K

x_1	U_{EXP}	U_{NOM}	U_{IMP}	U_{VDV}	U_{JUN}	U_{RAO}	U_{CFT}	U_{FLT}	U_{SPT}
Ethyl lactate (1) + Cyclohexanone (2)									
0.0000	1388.34	1388.34	1388.34	1388.34	1388.34	1388.34	1388.34	1388.34	1388.34
0.0915	1376.19	1375.25	1375.75	1375.15	1374.47	1376.36	1376.70	1383.33	1376.19
0.1848	1363.85	1362.25	1363.12	1362.07	1360.88	1364.22	1364.83	1376.07	1363.85
0.2798	1351.33	1349.32	1350.47	1349.11	1347.55	1351.93	1352.74	1366.77	1351.33
0.3767	1338.68	1336.48	1337.80	1336.25	1334.49	1339.47	1340.42	1355.64	1338.68
0.4755	1325.91	1323.72	1325.09	1323.49	1321.67	1326.84	1327.85	1342.87	1325.91
0.5762	1313.06	1311.04	1312.36	1310.83	1309.10	1314.05	1315.04	1328.67	1313.06
0.6790	1300.14	1298.45	1299.60	1298.27	1296.77	1301.09	1301.96	1313.21	1300.14
0.7838	1287.16	1285.93	1286.81	1285.80	1284.67	1287.95	1288.63	1296.70	1287.16
0.8908	1274.16	1273.49	1273.99	1273.43	1272.80	1274.63	1275.03	1279.29	1274.16
1.0000	1261.14	1261.14	1261.14	1261.14	1261.14	1261.14	1261.14	1261.14	1261.14
Ethyl lactate (1) + Cyclohexylamine (2)									
0.0000	1397.74	1397.74	1397.74	1397.74	1397.74	1397.74	1397.74	1397.74	1397.74
0.1001	1383.69	1383.66	1381.74	1382.40	1382.40	1383.64	1384.06	1387.82	1383.69
0.2002	1369.58	1369.67	1366.34	1367.47	1367.48	1369.64	1370.38	1377.09	1369.58
0.3002	1355.49	1355.77	1351.51	1352.95	1352.96	1355.74	1356.71	1365.49	1355.49
0.4003	1341.48	1341.98	1337.20	1338.81	1338.82	1341.94	1343.04	1353.02	1341.48
0.5003	1327.60	1328.27	1323.41	1325.03	1325.05	1328.23	1329.38	1339.69	1327.60
0.6003	1313.89	1314.66	1310.09	1311.61	1311.62	1314.62	1315.72	1325.51	1313.89
0.7002	1300.36	1301.14	1297.22	1298.52	1298.53	1301.11	1302.07	1310.51	1300.36
0.8002	1287.06	1287.71	1284.79	1285.76	1285.76	1287.69	1288.42	1294.75	1287.06
0.9001	1273.98	1274.38	1272.77	1273.30	1273.30	1274.37	1274.78	1278.28	1273.98
1.0000	1261.14	1261.14	1261.14	1261.14	1261.14	1261.14	1261.14	1261.14	1261.14
Ethyl lactate (1) + Cyclohexanone (2)									
0.0000	1443.13	1443.13	1443.13	1443.13	1443.13	1443.13	1443.13	1443.13	1443.13
0.0928	1422.85	1424.19	1424.92	1423.99	1422.41	1425.54	1426.17	1430.89	1422.85
0.1872	1403.08	1405.42	1406.71	1405.07	1402.32	1407.82	1408.96	1417.39	1403.08
0.2830	1383.80	1386.81	1388.51	1386.37	1382.83	1389.96	1391.48	1402.54	1383.80
0.3805	1364.99	1368.37	1370.30	1367.87	1363.92	1371.96	1373.73	1386.32	1364.99
0.4795	1346.63	1350.09	1352.10	1349.59	1345.56	1353.83	1355.70	1368.72	1346.63
0.5801	1328.72	1331.98	1333.91	1331.51	1327.72	1335.56	1337.38	1349.76	1328.72
0.6825	1311.22	1314.03	1315.71	1313.62	1310.38	1317.16	1318.78	1329.47	1311.22
0.7865	1294.14	1296.24	1297.52	1295.94	1293.51	1298.62	1299.88	1307.90	1294.14
0.8924	1277.45	1278.61	1279.33	1278.44	1277.11	1279.95	1280.67	1285.11	1277.45
1.0000	1261.14	1261.14	1261.14	1261.14	1261.14	1261.14	1261.14	1261.14	1261.14

APPLICATION

This study helps in making critical assessment of various theories of liquid mixtures. The thermodynamic properties of a binary mixture such as speed of sound and density are important for practical and theoretical points of view to understand liquid theory. Their properties are extremely useful for the design of process equipment in chemical industries and the data on some of the properties associated with the liquids and liquid mixtures like speed of sound and density find extensive application in solution theory and molecular dynamics.

CONCLUSION

In this paper, experimental speed of sound and density data is reported for binary mixtures of ethyl lactate with cyclohexanone, cyclohexylamine and cyclohexanol at a temperature of 303.15 K. From this experimental data, molar volume, isentropic compressibility and mean free length are computed, which are useful in the computation of speeds of sound by various models. Among the eight

theoretical models applied to predict the speeds of sound in the binary liquid mixtures under study, the speeds of sound computed using scaled particle theory are in close agreement with the experimental values for all the three binary liquid mixtures under investigation.

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