Indian Journal of Chemistry
Vol. 62, September 2023, pp. 962-969
DOI: 10.56042/ijc.v62i9.5361

Ultrasonic study for the molecular interactions of the ternary liquid mixture of *p*-anisaldehyde (4-methoxy benzaldehyde) with dimethylamine (N-methylmethanamine) and *n*-hexane at various temperatures

Y Geetha[a], P S Syed Ibrahim*[b], J Edward Jeyakumar[c] & S Chidambara Vinayagam[d]

[a] Department of Chemistry, Chennai Institute of Technology, Chennai 600 069, India
[b] Department of Chemistry, V.S.B Engineering College, Karur 639 111, India
[c] Department of Chemistry, DMI College of Engineering, Chennai 600 123, India
[d] RV Government Arts College, Chengalpattu 603 001, Tamil Nadu, India
Email: syedibuji@gmail.com

Received 24 November 2022; accepted(revised) 18 August 2023

The thermo-physical parameters like density (ρ), ultrasonic velocity (u) and viscosity (η) have been experimentally measured for the ternary liquid mixture of *para*-anisaldehyde (4-methoxy benzaldehyde) in *n*-Hexane solution with dimethylamine at various temperatures such as 303 K, 308 K and 313 K and at fixed frequency of 2 MHz. The thermodynamic and acoustical parameters such as adiabatic compressibility (β), internal pressure (π_i), cohesive energy (CE), free volume (V_f), free length (L_f), acoustic impedance (z), viscous relaxation time, Lennard Jones potential (LJP), and K value have been calculated from the experimental data. The various excess properties including excess acoustic impedance (Z^E), excess free length (L_f^E), excess adiabatic compressibility (β^E), excess free volume (V_f^E), excess ultrasonic velocity (U^E) and excess internal pressure (π_i^E) have also been computed from the calculated values. The values of U^E, Z^E, and L_f^E for each mixture have been fitted to the Redlich – Kister polynomial equation. The variation of these parameters with respect to different concentration at different temperatures for the ternary system of *para*-anisaldehyde + dimethylamine + *n*-hexane has been studied in accordance with their strength of molecular interaction under the influence of ultrasonic wave of frequency 2 MHz.

Keywords: Adiabatic compressibility, Viscous relaxation time, Excess ultrasonic velocity, Excess internal pressure

Ultrasonic studies on molecular interactions of binary and ternary liquid mixtures assume greater significances in current scenario[1]. The role of material science occupies unavoidable position in today's industrial and its ancillary plants growth. Thus, in chemical process industries, the raw materials and other materials possess fluid form because of which the physical, chemical and transport properties of the substances assume essential attractions by the physicists, chemists and research scholars. Consequently, the thermo-acoustical properties and thermodynamic properties of the organic liquid mixture vary due to molecular interactions which are due to dipole-dipole, dipole-induced dipole, induced dipole-induced dipole, weak Vander Waal's forces and hydrogen bonded interactions. The properties such as density, viscosity and ultrasonic velocity which are measured for the present study find extensive applications in solution theory and molecular dynamics[2].

The ternary liquid mixture contains an electron donor, an acceptor and an inert solvent. In this present study, the donor is *para*-anisaldehyde (4-methoxy benzaldehyde) (4MBA), an interesting compound which possess important physical and chemical properties, in fact, which stimulates the authors to undertake the current investigation. 4MBA is present in synthetic aircraft turbine oil which is used in gas turbine aircraft engines[3] and it is a clear, colourless liquid with a strong aroma which is found in anise and similar in structure to vanillin. Commercial use of 4MBA includes the preparation of vanilla, spices, apricot, butter, cinnamon, chocolate, caramel, cherry and walnuts *etc*. It is also used in thin layer chromatographic techniques and used for the manufacture of anti-microbial drugs in pharmaceutical industries[4]. Another component in the system under study is dimethylamine (DMA), which is also an important compound used in process/fields like vulcanization of rubber, agrichemicals and pharmaceuticals *etc*. In addition, DMA is indirectly used in the preparation of chemical weapon called tabun and in rocket fuels[5,6]. The medium in this present study is n-hexane which is a good non polar solvent, used in the

separation techniques. The present study involves the computation of acoustic, excess and thermodynamic parameters which are arrived from the experimentally observed values that have been used to understand different kinds of association, the molecular packing, molecular motion and various types of intermolecular interactions and their strength[7-11]. Excess parameters play a vital role in assessing the compactness due to molecular arrangement and the extent of molecular interactions in the liquid mixtures[12]. The physical (or) chemical nature and the corresponding strength of the molecular interaction between the components of the ternary liquid mixtures have been successfully investigated by the ultrasonic method[13]. The literature survey reveals that the binary mixtures consisting 4MBA and cresol/toluene/xylene/mesitylene/alkoxy ethanol/benzene *etc*., and a little extent only ternary mixtures consisting 4MBA as one of the components are already reported and hence the present probe has been focused on ternary mixture consisting 4MBA with DMA in n-hexane medium at various temperatures. In addition, the author aims to provide a holistic approach to the ternary system which is under investigation, in such a way that correlating the applications of both 4MBA and DMA in a novel manner since both are directly or indirectly used in the field of aerospace engineering.

Experimental Section

Materials

The mixtures of various equimolar concentrations ranging from 0.001 M to 0.01 M of the ternary system containing 4MBA with DMA and n-Hexane were prepared by taking analytical reagent grade and spectroscopic reagent grade chemicals with minimum assay of 99.9%. All the liquids were purified by the standard methods[14,15]. The procurement details are provided in Table 1.

Apparatus and Techniques

The density and viscosity were measured for various concentrations *viz*. 0.001 - 0.01 M of the system at different temperatures 303 K, 308 K and 313 K in addition to ultrasonic velocity keeping fixed frequency of 2 MHz. Ultrasonic velocity measurements were taken using an ultrasonic interferometer (Model F-81, supplied by M/S Mittal Enterprises, New Delhi) with an accuracy of ± 0.1 ms^{-1}. Water at desired temperature 303 K/ 308 K/ 313 K is circulated through the outer jacket of the double-walled measuring cell of the interferometer containing the experimental mixture. The interferometer was calibrated using the speed of sound of water at 298.15 K. A cell with 2 MHz. frequency was used to measure the speed of sound. The cell was filled with 8 to 10 ml solution and was allowed for 30 minutes before taking the readings. Average of 10 readings was taken as a final value. The measured speed of sound value is accurate up to ± 0.05%. The precession of sound speed based on 10 readings was calculated as ± 0.02%. Separate temperature control water bath procured from Ragas Industries, Chennai, India is attached with Interferometer. The densities of the mixture were measured using a 10 ml specific gravity bottle by relative measurement method. The specific gravity bottle was kept for about 30 minutes in a thermo-stated water bath for minimizing the error in density with an accuracy of ±0.01 kgm^{-3} [16]. An Oswald viscometer (10 ml) with an accuracy of ±0.001 Nsm^{-2} was used for the viscosity measurement. The flow time was determined using a digital racer stopwatch with an accuracy of ± 0.1 s. The viscometer was kept for about 30 minutes in a thermo-stated water bath to minimize the thermal fluctuation in viscosity.

Theory and calculations

Formulae for the determination of Acoustical (normal) Properties and Thermodynamic properties:

Intermolecular free length (L_f), is calculated using the standard expression

$$L_f = KT\,\beta^{1/2} \qquad \ldots(1)$$

where, KT is a temperature dependent constant known as Jacobson constant {$K = (93.875 + 0.375\ T) \times 10^{-8}$} and β is the adiabatic compressibility that can be calculated from the speed of sound (u) and the density of the medium (ρ) as

$$\beta = (u^2\rho)^{-1} \qquad \ldots(2)$$

Table 1— CAS Registry Number of the chemicals and its procurement particulars

Sl. No.	Name of the component	CAS RN	Suppliers Name	Brand Name
1	n-Hexane	110-54-3	Chandanmal & Co., Chennai	E. Merck Ltd (India)
2	Dimethylamine	124-40-3		
3	*para*-Anisaldehyde or4 methoxy benzaldehyde (4MBA)	123-11-5		

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

$$V_f = (M_{eff}\, u/\, k\eta)^{1/2} \quad \ldots(3)$$

Expression for the determination of internal pressure π_i by the use of free volume is given by

$$\pi_i = bRT(K\eta/u)^{1/2}(\rho^{2/3}/M^{7/6}_{eff}) \quad \ldots(4)$$

here, b stands for cubic packing which is assumed to be 2 for liquids and K is a dimensionless constant independent of temperature and nature of liquids and its value is 4.281×10^9, T is temperature in Kelvin scale and M_{eff} is the effective molecular weight of the mixture.

The viscous relaxation time was obtained by using the relation

$$\tau = (4/3)\, \beta\, \eta \quad \ldots(5)$$

Gibbs energy is calculated from the relation

$$G = KT\ln(KT\tau/h) \quad \ldots(6)$$

where, τ is the viscous relaxation time, K the Boltzmann constant, T, the temperature in Kelvin scale and h is the Planck's constant.

Free energy of formation $\Delta G = -RT\ln K$

where K is the stability constant or formation constant

$\Delta S = (\Delta H - \Delta G)/T$

ΔH is calculated from the plot of ln K against (1/T)

The acoustic impendence is given by,

$$Z = u\rho \quad \ldots(7)$$

Lennard Jones Potential (LJP) is given by[17]

$$LJP = 6Vm/Va \quad \ldots(8)$$

where, Vm is the molar volume and Va is the available volume.

The following relation is used for calculating cohesive energy (CE) [18,19]

$$CE = \pi_i .Vm \quad \ldots(9)$$

In the above relation, π_i represents the internal pressure and K[20,21] is the stability constant which is given by

$$K = Y/(b-y)^2 \quad \ldots(10)$$

$Y = (a - k^{1/2}b)/(k - k^{1/2})$ in which k = x/y, x is the difference between u_{cal} and u_{obs} at lower concentration a, y is the difference between u_{cal} and u_{obs} at higher concentration b, u_{cal} is the ultrasonic velocity of the mixture calculated from the mole fraction of the components using additive principle.

Formulae for the determination of Excess Properties:

In order to study the non-ideality of the liquid mixtures, namely excess parameters (A^E) of all the acoustic parameter were computed by

$$A^E = Aexp - Aid \quad \ldots(11)$$

where $Aid = \sum nAiXi$,

where Ai is any acoustical parameters and Xi is the mole fraction of the liquid components *i.e.*, the excess parameters of the ultrasonic velocity, acoustic impedance, and intermolecular free length were computed using the equations

$$u^E = u - (x_1u_1 + x_2u_2 + x_3u_3) \quad \ldots(12)$$

$$Z^E = (\rho u) - (x_1u_1\rho_1 + x_2u_2\rho_2 + x_3u_3\rho_3) \quad \ldots(13)$$

$$L_f^E = \frac{k}{(u^2\rho)^{1/2}} - \left[\frac{x_1k}{(u_1^2\rho_1)^{1/2}} + \frac{x_2k}{(u_2^2\rho_2)^{1/2}} + \frac{x_3k}{(u_3^2\rho_3)^{1/2}}\right] \quad \ldots(14)$$

where, u and ρ denote the ultrasonic velocity and density for the mixture, u_1u_2 and u_3 and $\rho_1\rho_2$ and ρ_3 denote the ultrasonic velocities and densities for the pure components.

k is Jacobson's constant

The values of u^E, Z^E, and L_f^E for each mixtures have been fitted to the Redlich – Kister[22] polynomial equation

$$Y^E = x(1-x)\sum_{i=1}^{10} a_i(1-2x)^{i-1} \quad \ldots(15)$$

The values of the coefficients a_i were calculated by the method of least squares along with the standard deviation $\sigma(Y^E)$. The coefficients i is an adjustable parameter for the best fit of the excess functions.

$$\sigma(Y^E) = \left[\frac{\sum(Y_{expt} - Y_{cal})}{n-p}\right]^{1/2} \quad \ldots(16)$$

where, n is the number of experimental points, p is the number of parameters, and Y_{expt} and Y_{cal} are the experimental and calculated excess parameters.

The values of V_f^E is calculated using the following relation

$$V_f^E = x_1M_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2M_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) + x_3M_3\left(\frac{1}{\rho} - \frac{1}{\rho_3}\right) \quad \ldots(17)$$

where, x_1M_1, x_2M_2, x_3M_3 are equimolar solutions and molecular weights of components (4MBA, DMA, and *n*-hexane, respectively) and ρ_1, ρ_2, ρ_3 are densities of pure components (4MBA, DMA, and *n*-hexane, respectively) and ρ is the density of the system under investigation.

The values of β^E is calculated using the following relation

$$\beta^E = \beta_s - (x_1\beta_1 + x_2\beta_2 + x_3\beta_3) \quad \ldots(18)$$

where, $x_1, x_2, x_3,$ are equimolar solutions, β^E *is the* excess adiabatic compressibility, $\beta_1, \beta_2, \beta_3$ are the adiabatic compressibility of pure components (4MBA, DMA and *n*-hexane respectively), β_s is the adiabatic compressibility of the mixture.

Similarly excess internal pressures will also be calculated using the following relation.

$$\pi_i^E = bRT\left(K_\eta/u\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) - \left\{\begin{array}{c} bRT\left(\frac{K_\eta}{U_1}\right)^{1/2}\left(\frac{\rho_1{}^{2/3}}{M_{1_{eff}}^{7/6}}\right) + bRT\left(\frac{K_\eta}{U_2}\right)^{1/2}\left(\frac{\rho_2{}^{2/3}}{M_{2_{eff}}^{7/6}}\right) + \\ bRT\left(K_\eta/u_3\right)^{1/2}\left(\frac{\rho_3{}^{2/3}}{M_{3_{eff}}^{7/6}}\right) \end{array}\right\} \quad \ldots(19)$$

where, u, ρ, M are velocity, density and molecular weight of the system respectively and $u_1\rho_1$ M_1, $u_2\rho_2$ M_2, $u_3\rho_3$ M_3, are velocity, density and molecular weight of the pure components, respectively.

Results and Discussion

The experimental values of ultrasonic velocity, density and viscosity of ternary liquid mixtures of 4MBA + DMA + *n*-hexane at 303 K, 308 K, 313 K are presented in Table 2. By using these values, acoustical parameters like acoustic impedance, adiabatic compressibility, free length whose values are provided in Table 3; free volume, internal pressure, cohesive energy were represented in Table 4; viscous relaxation time, Lennard Jones potential, free energy and formation constant were determined and those values are given in Table 5. Also, excess properties such as acoustic impedance, adiabatic compressibility, free length have been computed and the values are provided in Table 6; similarly, excess free volume, excess internal pressure and excess ultrasonic velocity were given in Table 7. Table 8 shows the comparative study between the experimental values of velocity, density and viscosity of pure components present in the ternary liquid mixtures of 4MBA + DMA + *n*-hexane at 303 K, 308 K, 313 K and the corresponding values of velocity, density and viscosity of the pure components obtained through the literature and it is observed that most of the values are in good agreement with the literature values.

Further, the plots of concentration against acoustic impedance, adiabatic compressibility, free length, free volume, internal pressure, cohesive energy, molecular interaction parameter, viscous relaxation time, Lennard Jones potential, free energy and formation constant are illustrated in graphs (Fig. S1-S11), respectively. In the same way, the excess parameters like acoustic impedance, adiabatic compressibility, free length, free volume, ultrasonic velocity and internal pressure were provided in Fig. S12-S17, respectively.

From the Table 2, it is observed that the ultrasonic velocity and viscosity increases with concentration at all the temperatures. This trend shows the strong interaction exists in between the components[23]. At the same time the velocity, viscosity and density decreases

Table 2 — Experimental values of velocity, viscosity and Density for 4MBA + DMA + *n*-hexane

Sl.No.	Conc. (M) X10^{-3}	Velocity (U) ms^{-1}			Viscosity (η)Nsm^{-2} x 10^{-4}			Density (ρ) Kgm^{-3}		
		303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
1	1	1634	1628	1618	1.8017	1.5675	1.2978	1.1270	1.0987	0.9387
2	2	1642	1631	1622	1.9261	1.6580	1.3429	1.1180	1.0876	0.9872
3	3	1655	1645	1624	2.0651	1.7275	1.4876	1.0967	1.0546	0.9148
4	4	1667	1653	1631	2.1924	1.8233	1.5344	1.0786	1.0324	0.9073
5	5	1673	1667	1639	2.2411	1.9857	1.6987	1.0187	1.0184	0.9011
6	6	1689	1678	1645	2.3912	2.0967	1.6432	0.9867	0.9256	0.8936
7	7	1695	1685	1654	2.4205	2.1379	1.7654	0.9634	0.9187	0.8830
8	8	1707	1699	1667	2.5672	2.2977	1.8976	0.9419	0.8974	0.8735
9	9	1718	1705	1671	2.6888	2.3653	1.9345	0.9197	0.8629	0.8672
10	10	1727	1719	1683	2.8016	2.4588	2.0987	0.8976	0.8718	0.8543

Table 3 — Calculated values of excess acoustic impedance, adiabatic compressibility and free length for 4MBA + DMA + *n*-hexane

S.No.	Conc. (M) x 10^{-3}	Acoustic Impedance(Z) x10^{+5} Kg/(m^2s)			Adiabatic compressibility(β) x 10^{-9} $N^{-1}m^2$			Free length (L_f) Å		
		Temperature (K)			Temperature (K)			Temperature (K)		
		303	308	313	303	308	313	303	308	313
1	1	1.82	1.78	1.63	3.38	3.43	3.98	1.14	1.15	1.20
2	2	1.81	1.77	1.52	3.39	3.45	3.75	1.14	1.15	1.20
3	3	1.78	1.73	1.51	3.45	3.50	3.99	1.15	1.16	1.21
4	4	1.75	1.70	1.51	3.48	3.54	3.96	1.16	1.17	1.23
5	5	1.71	1.69	1.50	3.65	3.53	3.96	1.18	1.20	1.23
6	6	1.62	1.55	1.45	3.74	3.83	3.92	1.20	1.21	1.23
7	7	1.59	1.54	1.40	3.79	3.83	3.94	1.21	1.21	1.24
8	8	1.57	1.52	1.36	3.82	3.86	3.92	1.21	1.22	1.24
9	9	1.53	1.47	1.33	3.89	3.98	3.90	1.22	1.24	1.24
10	10	1.51	1.41	1.27	3.93	4.11	3.92	1.23	1.25	1.26

Table 4 — Calculated values of free volume, internal pressure, cohesive energy and interaction parameter for 4MBA + DMA + *n*-hexane

Conc. (M) x 10^{-3}	Free volume x10^{-7} m^3/mol			Internal Pressure x10^8 Nm^{-2}			Cohesive Energy $kJMol^{-1}$			Molecular interaction parameter χ		
	Temperature (K)			Temperature (K)			Temperature (K)			Temperature (K)		
	303	308	313	303	308	313	303	308	313	303	308	313
1	2.43	3.02	4.03	20.8	19.0	15.6	15.9	14.9	14.2	0.176	–0.135	–0.179
2	2.20	2.78	3.86	21.4	19.4	16.3	16.5	15.4	14.3	0.169	–0.128	–0.172
3	1.99	2.65	3.35	21.8	19.3	16.2	17.2	15.8	15.3	0.168	–0.125	–0.185
4	1.83	2.47	3.24	22.2	19.5	16.3	17.8	16.3	15.6	0.183	–0.117	–0.182
5	1.79	2.20	2.79	21.5	20.1	17.1	18.2	17.0	16.4	0.156	–0.111	–0.165
6	1.63	2.05	2.98	21.7	19.3	16.6	19.0	18.0	16.1	0.181	–0.121	–0.155
7	1.61	2.00	2.69	21.5	19.4	17.0	19.2	18.2	16.7	0.188	–0.099	–0.147
8	1.49	1.82	2.44	21.7	19.7	17.5	19.9	18.9	17.3	0.195	–0.095	–0.154
9	1.40	1.75	2.39	21.8	19.4	17.5	20.5	19.4	17.5	0.205	–0.088	–0.148
10	1.33	1.67	2.14	21.8	19.1	18.0	21.0	20.0	18.2	0.201	–0.085	–0.145

Table 5 — Calculated values of viscous relaxation time, Lennard Jones potential, free energy internal pressure and K value for 4MBA + DMA + *n*-hexane

Con (M) x 10^{-3}	Viscous relaxation time (s) x 10^{-13}			Lennard Jones Potential (LJP) nJ mol^{-1}			Gibbs free energy ΔG $kJMol^{-1}$			$Kdm^{-3}mol^{-1}$		
	Temperature (K)			Temperature (K)			Temperature (K)			Temperature (K)		
	303	308	313	303	308	313	303	308	313	303	308	313
1	8.14	7.18	6.91	5.46	3.55	2.95	4.27	4.23	4.22	103	82.6	71.9
2	8.73	7.64	6.73	4.49	3.22	2.41	4.29	4.25	4.22	58.6	44.7	40.8
3	9.52	8.07	7.92	4.13	2.26	1.87	4.31	4.27	4.26	57.4	40.3	33.2
4	10.21	8.62	8.11	3.22	1.94	1.56	4.33	4.29	4.27	43.1	38.6	31.6
5	10.92	9.36	8.98	2.59	1.56	1.44	4.35	4.31	4.29	38.7	32.4	28.7
6	11.91	10.07	8.53	2.26	1.36	1.20	4.37	4.33	4.28	30.5	28.7	25.6
7	12.20	10.09	9.28	1.91	1.25	1.14	4.38	4.35	4.3	29.8	28.8	23.8
8	13.10	11.81	9.94	1.56	1.09	1.02	4.41	4.37	4.32	27.2	25.6	20.1
9	14.01	12.61	10.1	1.48	1.04	0.94	4.41	4.39	4.35	25.5	23.3	19.4
10	14.71	13.50	11.1	1.28	0.93	0.88	4.43	4.41	4.38	------	------	------

at all the concentrations while the temperature increases which is due to thermal agitation of the molecules. Further, the decrease in ultrasonic velocity may be attributed to the rupture of intermolecular hydrogen bonding in p. anisaldehyde as well as the dissociation of dipolar association which operates in between 4MBA and DMA. This is in accordance with the report provided by Rathnam *et al*[24].

From the Table 3, the increasing tendency of internal pressure with increase in temperature maintains the

Table 6 — Computed values of excess acoustic impedance, adiabatic compressibility and free length for 4MBA + DMA + *n*-hexane

S. No.	Conc. (M) x10^{-3}	Excess Acoustic Impedance(Z^E) Kg/(m^2s)			Excess Adiabatic compressibility(β^E)x$10^{-7}N^{-1}m^2$			Excess Free length (L^E_f) Å		
		Temperature (K)			Temperature (K)			Temperature (K)		
		303	308	313	303	308	313	303	308	313
1	1	867.11	877.12	885.2	–8.93	–9.34	–9.67	–5.12	–5.17	–5.22
2	2	861.01	875.9	884.2	–8.86	–9.28	–9.54	–5.12	–5.16	–5.23
3	3	865.05	873.9	882.9	–8.78	–9.11	–9.48	–5.11	–5.15	–5.22
4	4	861.05	872.9	879.4	–8.70	–9.02	–9.36	–5.10	–5.15	–5.21
5	5	862.99	871.2	878.6	–8.60	–8.93	–9.25	–5.10	–5.15	–5.21
6	6	859.97	870.4	876.4	–8.49	–8.86	–9.19	–5.10	–5.13	–5.20
7	7	864.94	869.3	874.3	–8.37	–8.74	–9.06	–5.08	–5.12	–5.20
8	8	861.92	868.3	873.1	–8.23	–8.62	–8.92	–5.08	–5.12	–5.19
9	9	863.96	865.5	872.8	–8.07	–8.56	–8.88	–5.07	–5.12	–5.18
10	10	860.87	863.9	871.6	–7.89	–8.47	–8.73	–5.06	–5.11	–5.17

Table 7 — Computed values of excess free volume, excess ultrasonic velocity and excess internal pressure for 4MBA + DMA + *n*-hexane

S. No.	Conc.(M) x10^{-3}	Excess Free Volume(V_f^E) x10^{-8} (m^3/mol)			Excess ultrasonic velocity(U^E) (m/s)			Excess Internal Pressure x10^8Nm^{-2}		
		Temperature (K)			Temperature (K)			Temperature (K)		
		303	308	313	303	308	313	303	308	313
1	1	–2.63	–2.79	–2.96	–121.5	–119.8	–111.9	–2.97	–2.99	–2.99
2	2	–2.08	–2.76	–2.87	–126.07	–117.3	–108.5	–3.65	–3.71	–3.78
3	3	–2.06	–2.74	–2.88	–111.9	–116.3	–106.4	–3.66	–3.72	–3.79
4	4	–2.05	–2.65	–2.75	–120.2	–115.9	–105.3	–3.67	–3.74	–3.76
5	5	–2.05	–2.55	–2.63	–104.04	–112.6	–104.9	–3.69	–3.70	–3.75
6	6	–2.04	–2.48	–2.58	–99.56	–109.6	–103.8	–3.71	–3.77	–3.74
7	7	–2.02	–2.37	–2.44	–94.76	–101.8	–99.8	–3.78	–3.73	–3.72
8	8	–1.99	–2.27	–2.39	–91.54	–99.2	–91.9	–3.79	–3.70	–3.71
9	9	–1.96	–2.19	–2.27	–86.58	–92.6	–87.4	–3.72	–3.71	–3.71
10	10	–1.94	–2.05	–2.19	–81.77	–88.9	–83.5	–3.75	–3.73	–3.67

Table 8 — Comparative study between Literature values and Observed values of Velocity, Viscosity and Density for the pure components present in the ternary system at working temperatures

Sl No.	Name of the pure component in the mixture		Velocity (U) ms^{-1}			Viscosity (η)Nsm^{-2} x 10^{-4}			Density (ρ) Kgm^{-3}		
			303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
1.	n-Hexane	L	1058.3 [35]	nda	nda	0.296 [36]	nda	nda	0.654 [37]	nda	nda
		O	1066	1041	1025	0.312	0.303	0.299	0.644	0.638	0.622
2.	DMA	L	nda	nda	1433 @	0.340#	nda	nda	0.827 @	nda	nda
		O	1678	1527	1412	1.81	1.78	1.74	0.707	0.699	0.707
3.	4MBA	L	nda	nda	nda	nda	nda	nda	nda	nda	nda
		O	1079	1068	1057	1.802	1.744	1.693	1.12	1.008	0.997

nda: no data available#source: www.inchem.org>documents>icsc>eics>1485
@ flexim news update 17: a new perspective:17/2017 p5
L: Literature values
O: Observed values

existing interaction between *para*-anisaldehyde and dimethylamine. The changes of Lenard Jones potential were observed in the present system for all temperatures. The decreasing value of LJP with increase in temperature as well as concentration shows the complex formation or hydrogen bonding between the components. Adiabatic compressibility, free length and free volume were decreasing with concentration. It shows the compactness of the liquid mixture with strong interactions.

Table 9 — Computed values of enthalpy, free energy of formation and entropy for 4MBA + DMA + *n*-hexane

Con. (M) X 10^{-3}	Enthalpy ΔH kJMol^{-1}			Free energy of formation ΔG* kJMol^{-1}			Entropy ΔS JMol^{-1}		
	Temperature (K)			Temperature (K)			Temperature (K)		
	303	308	313	303	308	313	303	308	313
1	–38.30	–37.92	–37.75	–11.68	–11.31	–11.13	–126.35	–123.09	–120.56
2	–36.87	–36.35	–36.27	–10.26	–9.74	–9.66	–121.66	–117.99	–115.85
3	–36.82	–36.08	–35.73	–10.21	–9.47	–9.12	–121.49	–117.12	–114.13
4	–36.10	–35.97	–35.60	–9.49	–9.36	–8.99	–119.11	–116.76	–113.72
5	–35.83	–35.52	–35.35	–9.21	–8.91	–8.74	–118.21	–115.31	–112.92
6	–35.23	–35.21	–35.06	–8.61	–8.6	–8.44	–116.23	–114.30	–111.97
7	–35.17	–35.22	–34.86	–8.56	–8.61	–8.25	–116.04	–114.33	–111.36
8	–34.94	–34.92	–34.43	–8.33	–8.31	–7.81	–115.28	–113.35	–109.96
9	–34.77	–34.68	–34.33	–8.16	–8.07	–7.72	–114.74	–112.57	–109.66
10	------	------	------	------	------	------	------	------	------

Table 10 — Mean values of stability constant, enthalpy, free energy of formation and entropy for 4MBA +DMA+ *n*-hexane

	K dm^{-3}mol^{-1}			ΔH kJMol^{-1}			ΔG* kJMol^{-1}			ΔS JMol^{-1}		
	Temperature (K)			Temperature (K)			Temperature (K)			Temperature (K)		
	303	308	313	303	308	313	303	308	313	303	308	313
Mean value	46.1	38.3	32.8	–36.00	–35.77	–35.48	–9.48	–9.20	–8.90	–118.79	–116.09	–113.35

The internal pressure is important factor in deciding thermodynamic properties. The internal pressure is the cohesive force which is the resultant of force of attraction and force of repulsion between the molecules. The solubility property of solvent-solute interaction is arrived from the internal pressure which is due to hydrogen bonding, van der walls forces, columbic forces and formation of charge transfer complexes.

The sign of excess parameter reveals the compactness due to molecular rearrangement and the extent of molecular interaction in ternary liquid mixtures. The excess values are given in Tables 6 and 7. The negative values of excess parameters reveal that the maximum interactions are present in the system[25-28]. According to Sri Devi *et al*.[29], negative excess values are owing to closely packed molecules which supports the existence of strong molecular interactions and the positive values predict weak interactions between the components. The negative value of excess free length and excess adiabatic compressibility reported that the strong dipole-dipole interactions[30] in ternary liquid mixtures. Additionally, the negative value of excess free volume and excess internal pressure attributed to the strong hydrogen bond between the components. Thermodynamical parameters also proved that the strong interaction exist between the components (Tables 9 and 10). Formation constant for the present system decreases with increase in temperature. This trend supports the fact that at lower temperature inter/intra molecular hydrogen bonding exists in between PA and DMA but at the same time, at higher temperature the hydrogen bonding gets ruptured due to the thermal agitation of the molecules. Viscous relaxation time shows that the same type of complex formed at all temperatures.

In this present study, the negative values are recorded for β^E which is due to the closely packed molecules that causes strong interaction between the molecules. Similar conclusions were also drawn by Islam and Quadri[31]. The values of β^E found to decrease while the concentration increases at all the temperatures whereas the β^E values increases gradually when the temperature increases that shows the linear behaviour which confirms the specific interaction of the system. The corresponding values are tabulated in Table 6 and the Fig. is provided in Fig.S12. Similarly, negative values are obtained for π_i^E due to the strong dipole-dipole interactions through the hydrogen bonding in between the 4MBA and DMA in n-hexane medium.

The formation constant (stability constant) K is calculated using the method of Kannappan equation[32-34]. By determining the values of K at various temperatures, the thermodynamic stability of the donor-acceptor complex formed between 4MBA and DMA will be assessed. The stability constant value decreases with increase in temperature in this present study. The values of stability constant depend upon

the structure of 4MBA and DMA. In this present study, the donor is 4MBA in which the electron donating group is present at *para* position which causes change in the values of stability constant which is independent upon the concentration. The thermodynamic parameters namely enthalpy change, entropy change and free energy change are determined for the donor-acceptor complexes. The enthalpy change values are found to be negative which may be obtained from the straight line of the plot drawn in between ln K and 1/T (Fig. S18). The plot seems to be involving linear change. Therefore, the complex formation follows the exothermic reaction. The trend in the values of free energy change supports the stability constant values. The entropy change values are also negative.

Conclusion

Acoustical parameters/thermodynamical parameters and excess parameters strongly showed the presence of sensitive interaction between the components. The negative value of molecular interaction is also very good evidence for the strong interaction that exists at 308 K and 313 K in ternary liquid mixtures due to dipole-dipole, dipole-induced dipole, weak van der Waals forces and intermolecular hydrogen bonding in between the 4MBA and DMA. At the same time, mild interaction is observed at 303 K which may be because of the positive values of molecular interaction parameter obtained in this present study. Hence the present study advocates the usage of 4MBA along with DMA in rocket fuels in very smaller proportion.

Supplementary Information

Supplementary information is available in the website: http://nopr.niscpr.res.in/handle/123456789/58776.

References

1 Ewing M B, Levian, B J & Marsh K N, *J Chem Thermodynamics,* 2 (1970) 689.
2 Mchaweh A, Alsaygh A & Moshfeghian, M A, *Fluid Phase Equilibria*, 224 (2004) 157.
3 BaskaranR & Kubendran T R, *J Thermo-Phy Heat Transfer*, 25 (2011) 614.
4 Kolla Narendra, *Studies of molecular interactions in binary mixtures of anisaldehyde with arenes and cresols at different temperatures,* Ph D thesis, (Acharya Nagarjuna University, Nagarjuna Nagar, AP, India) 2012.
5 Gysel A B V & Musin W, *Methylamines*, (Wiley-VCH Verlag, Weinheim), 2005.(https://doi.org/10.1002/14356007.a16_535)
6 Robert D. Ashford, *Ashford's Dictionary of Industrial Chemicals,* 3rd ed. (2011) 3284. ISBN:0952267438, 9780952267430
7 Sumathi T & Uma Maheswari J, *Indian J Pure Appl Phys***,** 47 (2009) 782.
8 Rama Rao G V, *Indian J Pure Appl Phys*, 42 (2004) 826.
9 Narendra K, *E-Journal of Che.,*7 (3) (2010) 927. https://doi.org/10.1155/2010/536784.
10 Ali A & Nain A K, *Indian J Pure Appl Phys,* 39 (2001) 421.
11 Anwar, *J Chinese Chem Soc,* 51 (2004) 477.
12 Tadkalkar A P, *Archives Phy Res,* 3(2012) 287.
13 Arul G & Palaniappan L, *Indian J Pure Appl Phys,* 43 (2005) 755.
14 Suryanarayanan C V & Kuppusamy J, *J Acoust Soc Ind.*, 4 (1976) 75.
15 Suryanarayanan C V, *Indian J Chem,* 25A (1986) 538.
16 Robert Weust C, *CRC Handbook of chemistry & physics,* 52nd ed. (The Chemical Rubber Co) 1971.
17 Sodzhievi, *Archives Acoustics,* 2 (1977) 325.
18 Arun P, Natarajan S & Suryanarayana C V, *Indian J Tech,* 29 (1991) 537.
19 Rajendran V, *Indian J Pure Appl Phys*, 34 (1996) 52.
20 Marwein B L & Bhatt SN, *Thermochimica Acta*, 118 (1987) 277.
21 Kannappan V, Jaya Shanthi R & Malar E J P, *Phys Chem Liq,* 40 (2005) 507.
22 Redlich O & Kister A T, *Ind Eng Chem*, 40 (1948) 345.
23 Vibhu I, Singh A K, Gupta M & Shukla J P, *J Mol Liq,* 115 (2004) 1.
24 Shantilaloswal, Manapragada & Rathnam V, *Can J Chem* 62 (1984) 2851.
25 Ali A, Nain A K, Sharma V K & Ahmad S, *Phy Chem Liq,* 42 (2004) 375.
26 Zorebski E& Lubowiecka-Kostka B, *J Chem Thermodynamics*, 41 (2009) 197.
27 Raj A M E, Resmi L B, Jothy V B, Jayachandran M & Sanjeeviraja C, *Fluid Phase Equilibria*, 281 (2009) 78.
28 Mosterio L, Casas L M & Legido J L, *J Thermodynamics,* 41 (2009) 695.
29 Sri Devi U, Samatha K & Visvanantasarma A, *J Pure Appl Ultras,* 26 (2004) 1.
30 Patwari M K, Bachi R K, Sathyanarayana B & Nallani S, *J Chem Eng Data,* 54 (2009) 1069.
31 Islam M R & Quadri, *Thermochimica Acta,* 115 (1987) 335.
32 Kannappan V & Kothai S, *J Acoust Soc India*, 30 (2002) 76.
33 Kannappan V & KothaiS, *Advances Ultrasonics,* 124 (2001).
34 Kannappan V & Kothai S, *Ind J Pure & Appl Physics,* 40 (2002) 17.
35 Kannappan V & Indra Gandhi N, *Phys Chem Liq,* 46 (2008) 510.
36 Marsh K N, *TRC Thermodynamics Tables Hydrocarbons*, (Thermodynamics Research Centre, The Texas A & M University system, College station, Texas) 1989. (https://www.worldcat.org/title/476424418?oclcNum=476424418)
37 Riddick J A, Bunger W B & Sakano T, *Organic Solvents Techniques of Chemistry,* Vol 1, 4th ed., (John Wiley, New York) 1986.