Ultrasonic velocity and allied acoustical parameters of 2, 4-dinitrophenyl hydrazine based Schiff base in DMSO

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Novel 2, 4-dinitrophenyl hydrazine based Schiff bases (**L1-L3**) has been successfully synthesized and characterized. The ultrasonic velocity (C) and density (ρ) has been measured for the synthesized Schiff bases with DMSO (Dimethyl sulfoxide) solvents at 300 K. Using these experimental data ultrasonic Velocity, adiabatic compressibility, intermolecular free length and specific acoustic impedance have been evaluated. From the experimental data, it has been found that **L1** ascribed higher ultrasonic velocity as compared to other molecular probes **L2** and **L3**. The strength and nature of interaction between the molecular probes and DMSO solvents has been discussed. Scanning electron microscope studies of molecular probes are performed to discuss the microstructure and surface functionalities.

Keywords: Acoustical Parameters, Ultrasonic velocity, Adiabatic compressibility, Intermolecular free length, Specific acoustic impedance, Schiff base

Owing the interest of ultrasonic velocity and related acoustical parameters, it is noteworthy to design and synthesis of novel Schiff bases[1]. It is well know that, Schiff bases are known to be good ligands for metal ions. Apart from that, Schiff base ligands have played major role in efficient catalysts, sensors, nonlinear optics, DNA cleavage etc.[2] The several novel synthesized Schiff base have been found to possess considerable biological activities such as antibacterial, antitumor, and antidiabetic. Thus, study of their molecular interactions in solution will be useful to recognize the biological applications[3,4].

Ultrasonic is the branch of acoustic, it consists of waves of high frequencies. It is great interest because it is used for the study of molecular interactions in liquids[5]. Due to their unique properties, ultrasonic wave plays major role in producing significant information about the structure and properties of matter[6,7]. Owing their distinctive nature, ultrasonic technique is used to study the nature of molecular interaction in liquids, liquid mixture, stability of complexes and electrolyte solution etc.[8,9]. The ultrasonic velocity plays an important role in the examination of intermolecular interactions between the components of liquid mixtures. Apart from that, the ultrasonic velocity is a useful tool for used for

study of weak molecular interactions. The measurements of ultrasonic velocity have proved to be useful probe for generating the information regarding the degree of deviation from complex formation, internal structure, ideality and molecular interactions in liquids because of their accuracy[10-12]. In literature, it reveals that much work has been in water (protic) and mixtures of organic solvent such as protic-protic or protic-aprotic. From the literature, it ascribed that a few literatures are found the study of acoustic properties in mixtures of DMSO (dimethyl sulfoxide) -H_2O solvents, but no work has reported in pure DMSO[13]. From the literature, it is found that hydrazone derivatives were used in molecular sensor, metal organic frameworks and biomedical applications[14-16]. Further, as ultrasonic wave can interact with atomic and sub atomic levels with high penetration energy, the synthesized molecular probes have many novel characteristics without changing their elemental properties[17-20]. Being its non-destructive nature, it can produces hybrid characteristic in atomic level in a synthesized material or compounds, which can explore its brilliance when it is implemented for fabrication of different materials. To be best of our knowledge, herein, we wish to report the design, synthesis and

characterization of novel molecular probes (**L1-L3**) that belongs to a family of Schiff base derived from 2, 4-dintrophenyl hydrazine (Scheme 1) and systematic study of their ultrasonic velocity and related acoustical parameters. The densities and ultrasonic velocities of solutions of **L1**-**L3** were determined. From these values ultrasonic Velocity (C), adiabatic compressibility (β_s), intermolecular free length (L_f) and specific acoustic impedance (Z) were calculated.
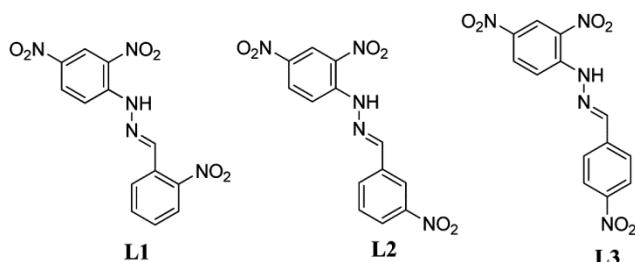
Materials and Methods

Materials

2-nitrobenzaldehyde, 3-nitrobenzaldehyde, 4-nitrobenzaldehyde and 2, 4-dintrophenyl hydrazines were obtained from Aldrich Chemical Company. The spectroscopic grade solvent used was obtained from Aldrich Chemical Company and used without further purifications. The ^{1}H NMR spectral data were recorded on Varian-AS 400 spectrometers. Infrared spectra obtained using Perkin-Elmer FTIR spectrophotometer (4000-400 cm^{-1}). The sound velocity of components was measured by ultrasonic interferometer (Mittal enterprises, model F-81s at variable frequency) at 2 MHz with frequency tolerance ± 0.03%. It consists of high frequency generator and a measuring cell. The viscosities and densities were measured by Ostwald's viscometer (accuracy ± 0.0004 N. m^{-2}.S) and specific gravity bottle (accuracy ± 0.03 kg.m^{-3}), respectively. The various acoustic parameters were calculated by using Micro Soft Excel programme and plotted by using Origin software. The compounds (**L1-L3)** were prepared by modifying reported procedures. All measurements were carried out by taking a solution (10^{-2} to 10^{-5} M in DMSO) of the corresponding ligands.

Preparation of Schiff bases (L1-L3)

The Schiff-base ligands were prepared by reaction of 2, 4-dintrophenyl hydrazines with one equivalent of corresponding nitrobenzaldehyde in DMSO at 80 °C for 8 h. The entire synthesis processes of molecular probes were schematically represented in the Scheme 2.

### *(E)-1-(2-nitrobenzylidene)-2-(2,4-dinitrophenyl)hydrazine) (L1)*

To a well-stirred solution of 2, 4-dintrophenyl hydrazine (0.39 g, 2 mmol) in DMSO, (50 ml) a solution of 2-nitrobenzaldehyde (0.32 g, 2 mmol) was added. The reaction mixture was stirred at 80 °C for 8 h. A yellow color precipitate (**L1**) was formed. The resulting mixture was filtered and dried in open air. Yield: 96%. ^{1}H NMR (400 MHz, DMSO-d$_6$): 11.96 (s, 1H), 9.08 (s, 1H), 8.97 (s, 1H), 8.86 (d, J = 2.6 Hz, 1H), 8.40 (dd, J = 9.6 Hz, 1H), 8.18 (dd, J = 16.4 Hz, 1H), 8.12 (m, 1H), 7.91 (m, 1H), 7.71 (t, J = 7.7 Hz, 1H).

(E)-1-(3-nitrobenzylidene)-2-(2,4-dinitrophenyl)hydrazine) (L2)

To a well-stirred solution of 2, 4-dintrophenyl hydrazine (0.39 g, 2 mmol) in DMSO, (50 ml) a solution of 3-nitrobenzaldehyde (0.32 g, 2 mmol) was added. The reaction mixture was stirred at 80 °C for 8 h. A yellow color precipitate (**L2**) was formed. The resulting mixture was filtered and dried in open air. Yield: 88%. ^{1}H NMR (400 MHz, DMSO-d$_6$): 11.81 (s, 1H), 8.98 (s, 1H), 8.74 (s, 1H), 8.57 (s, 1H), 8.49 (dd, J = 7.2 Hz, 2H), 8.17 (dd, J = 6.6 Hz, 2H), 7.83 (d, J = 8.2 Hz, 1H).

(E)-1-(3-nitrobenzylidene)-2-(2,4-dinitrophenyl)hydrazine) (L3)

To a well-stirred solution of 2, 4-dintrophenyl hydrazine (0.39 g, 2 mmol) in DMSO, (50 ml) a solution of 3-nitrobenzaldehyde (0.32 g, 2 mmol) was added. The reaction mixture was stirred at 80 °C for 8 h. A yellow color precipitate (**L3**) was formed. The resulting mixture was filtered and dried in open air. Yield: 90%. ^{1}H NMR (400 MHz, DMSO-d$_6$): 11.85

Scheme 1 —Structures of L1-L3 (used for study of acoustic parameters).
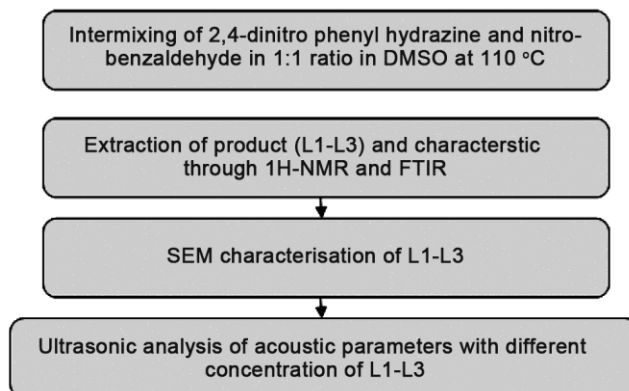
Scheme 2 — Synthesis processes of molecular probes L1-L3.

(s, 1H), 8.88 (s, 1H), 8.83 (s, 1H), 8.43 (d, J = 8.6 Hz, 1H), 8.40 (d, J = 7.2 Hz, 1H), 8.34 (d, J = 7.6 Hz, 2H), 8.18 (d, J = 6.4 Hz, 1H), 7.7 (d, J = 7.8 Hz, 1H).

Results and Discussion

Ultrasonic velocities and densities of molecular probes (**L1-L3**) were measured in DMSO. The experimental values of density (ρ), ultrasonic velocity (*C*) at 300 K along with the derived values are shown in Table 1. The values of ultrasonic velocity of **L1-L3** decrease with increase in concentration of **L1-L3** in DMSO as shown in Fig. 1. It may be due to the increase of solute-solvent interactions, cohesive forces and molecular associations such as dipole-dipole and dipole induced dipole between the molecular probes and DMSO solvent. However, gradually decrease the ultrasonic velocity with increase the concentration of molecular probe results that the formation of weak interaction between the molecular probes with solvent. The gradually increases in ultrasonic velocity shows there is a significant interaction between molecular probes and the solvent molecules suggesting the structure promoting behavior of added solute. A similar result was previously reported for carbohydrate in binary mixtures in DMSO-H_2O at room temperature[21]. Ultrasonic velocity is calculated by using Eqn (1),

$$C = fx\lambda \qquad \qquad \dots (1)$$

where, C is the ultrasonic velocity, f is frequency and λ is wavelength.

The adiabatic compressibility (β_s) plays a major role in evaluates the molecular rearrangement between the solute and solvent. The β_s is the important parameter that provides the essential information about physic-chemical behavior such as molecular association, dissociation and formation. The β_s decrease with increase the concentration of probes (**L1-L3**) may be attributed due to formation of weak interactions between the probes and solvent, thus it guided the long range disperses forces. Apart from that, solvent molecules play an important role in increase in the total internal pressure and thus solution becomes harder to compress. The β_s has been

Table-1 — Experimental ultrasonic velocity, adiabatic compressibility (β_s), Intermolecular free length (L_f) and Specific acoustic impedance (Z) of molecular probes (L1-L3) in DMSO

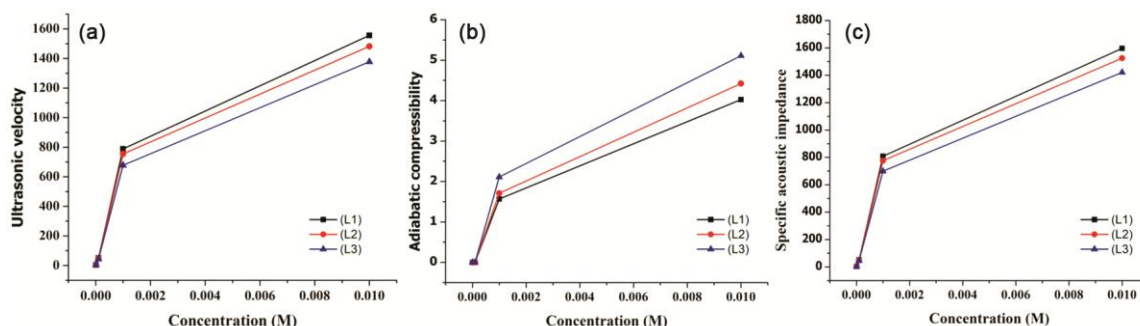| Acoustic parameters/ Molecular Probes		U S.velocity (C) (m.sec-1)	Adiabatic compressibility (β_s) (Pa^{-1})	Intermolecular free length (L_f) (m)	Specific acoustic impedance (Z) (N.m^{-2})
L1	0.01	1556	4.02563E-07	0.000041539	1596.456
(Conc in M)	0.001	788	1.56566E-06	0.000161557	808.488
	0.0001	50.2	0.0003	0.039909133	51.5052
	0.00001	3.74	0.00006	7.190126404	3.83724
L2	0.01	1482	4.42474E-07	0.000045657	1524.978
(Conc in M)	0.001	754	1.70939E-06	0.000176388	775.866
	0.0001	47.4	0.0004	0.044632892	48.7746
	0.00001	3.52	0.00007	8.093313975	3.62208
L3	0.01	1378	5.10791E-07	0.000052707	1420.718
(Conc in M)	0.001	678	2.11E-06	0.000217725	699.018
	0.0001	44	0.0005	0.05169673	45.364
	0.00001	3.12	0.00009	10.28156528	3.21672

Fig. 1 — Experimental (a) ultrasonic velocity; (b) adiabatic compressibility (β_s); (c) Specific acoustic impedance (Z) of molecular probes (L1-L3) in DMSO at different concentrations.

calculated by using the following equation, where 'C' is the ultrasonic velocity, 'ρ' is the density of the solutions.

$$\beta_s = 1/\rho C^2 \qquad \ldots (2)$$

The decrease in β_s with increase in the concentration suggests the noteworthy structural rearrangement in neighboring atmosphere of the ions.

From the data analysis, it was found that the decrease in β_s with increase in the concentration ascribed due to (i) physical: due to non-specific van der Walls type interactions; (ii) chemical: due to the formation of H-bond architecture, charge transfer forces and (3) structural: due to changes of interstitial accommodation and free volume. The effect of ultrasonic wave is ascribed in term of intermolecular free length (L_f). The L_f was measured by using the following equation

$$L_f = k\beta_s^{\frac{1}{2}} \qquad \ldots (3)$$

Where 'C' is the ultrasonic velocity, 'ρ' is the density of the solutions and 'k' is temperature dependent constant calculated by using the equation [93.875 + (0.375T)] $\times 10^{-8}$ with 'T' being the absolute temperature[7]. The L_f is the average distance between the surfaces of the two molecules. It demonstrates the information on how much they compressed in order to interact by decreasing the gap between the two atoms. From the calculation, it ascribe that the L_f decreases with increase in concentration of molecular probes, which clearly indicates the decrease in L_f between the

molecules due to stronger interaction between molecular probes with solvent molecules. From the data, it showed that the L_f increase with decrease in ultrasonic velocity. On the other hand, the β_s values increase with increase in the L_f and vice-versa.

The specific acoustic impedance (Z) is calculated by using the following equation

$$Z = Cx\rho \qquad \ldots (4)$$

Where 'C' is the ultrasonic velocity, 'ρ' is the density of the solutions. The Z is the complex ration of the effective sound pressure at a point to the effective particle velocity at that point. From the data analysis, it showed that the Z increase with increase in concentration of solute. It may be occurs due to the structural relaxation process. It occurred due to the electro-restriction effect. This types of phenomenon displayed due to the formation strong H-bond interactions between probes with DMSO as in Scheme 3.

Morphological analysis of molecular probes (L1-L3)

The morphology of molecular probes (**L1-L3**) are analyzed by scanning electron microscope (SEM). As revealed from Fig. 2a, **L1** shows the thin fibrous morphology with diameter of ~1 μm and several micrometers in length. Such type of structural appearance is also observed for molecular probe **L3** (Fig. 2c). However, a significant difference in morphology is viewed for the probe **L2**. An aggregated phase with particle size (~2 μm) showed by probe **L2** shown as Fig. 2b. A similar observation
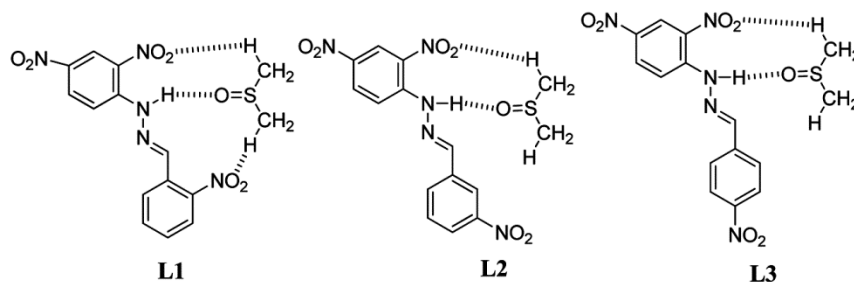
Scheme 3 — Schematic for plausible H-bond architecture between probes (L1-L3) with DMSO.
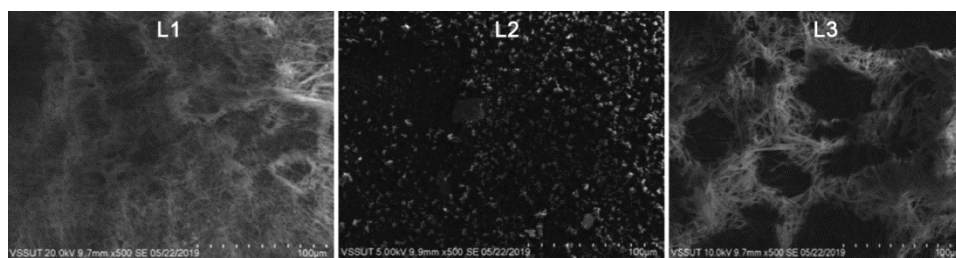

Fig. 2 — (a) SEM images of (a) L1, (b) L2 and (c) L3.

was previously reported for benzothiazole Schiff base metal complex[22]. The characteristics fibrous morphology for **L1** and **L3** may be related to the organized self-assembly of ligand molecules *via* various non-covalent interactions and resemblance with the gel fiber network of supra-molecular gelators[23]. More precisely, the observed morphology for **L3** may be strongly correlated with the flexible directional growth *via* non-covalent interactions due to less hindrance para-substituted nitro (-NO$_2$) groups. Such possibility is also favored for ortho-substituted nitro groups, but in case of meta-nitro substituted probe, such self-assembly is hampered. All the prepared organic ligands show the presence of three distinct elements, carbon, oxygen and nitrogen during their EDAX analysis (Supplementary Data). As expected the highest% is obtained from the carbon due to organic framework, while the elemental oxygen is came due to presence of nitro groups in organic structures.

Conclusions

The molecular probes were synthesized between 2, 4-dintrophenyl hydrazines and 2-nitrobenzaldehyde, 3-nitrobenzaldehyde and 4-nitrobenzaldehyde. The successful synthesized molecular probes were characterized by ^{1}H NMR, FTIR, Mass and SEM. The ultrasonic velocity and density along with their various thermodynamic parameters has been experimentally determined. It suggests that the stronger solute-solvent interactions are present may be due to the presence of hydrogen-bond interactions between molecular probes with DMSO solvent. The molecular probe **L1** shows excellent properties compared to other molecular probes due to the formation of strong H-bond architecture between O-atom of DMSO with -NH atoms of **L1**. SEM images of the ligands confirm the rearrangement and formation of new H-bonding, which are responsible for the brilliance of ligands for different industrial and scientific applications. The variation of different acoustic parameters computed from ultrasonic velocity data provides better information between the compositions of ligands. The computed characteristics of ligands confirm the implementation of ultrasonic technique is one of the novel methods for synthesis of such other ligands.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_59A (08) 1108-1112_SupplData.pdf.

References
1 (a) Bhalla V, Roopa & Kumar M. *Dalton Trans*, 42 (2013) 975; (b) Que E L, Domaille D W and Chang C J, *Chem Rev*, 108 (2008) 1517.
2 (a) Mizukami S, Okada S, Kimura S & Kikuchi K, *Inorg Chem*, 48 (2009) 7630; (b) Tamanini E, Flavin K, Motevalli M, Piperno S, Gheber L A, Todd M H & Watkinson M, *Inorg Chem*, 49 (2010) 3789; (c) Maruyama S, Kikuchi K, Hirano T, Urano Y & Nagano T, *J Am Chem Soc*, 124 (2002) 10650; (d) Carol P, Sreejith S & Ajayaghosh A, *Chem. Asian J*, 2 (2007) 338; (e) Dai Z & Canary J W, *New J Chem*, 31 (2007) 1708.
3 Seitz H K & Stickel F, *Nat Rev Cancer*, 7 (2007) 599.
4 Galluzzi L, Blomgren K & Kroemer G, *Nat Rev Neurosci*, 10 (2009) 481.
5 Herfeld K F & Litovitz, *Absorption and Dispersion of Ultrasonic Waves*, (Academic Press, New York), 1959.
6 Bhambi D, Jain S, Sharma R & Talesara G L, *Ind J Pharm Sci*, 69 (2007) 28.
7 Jacobson B, *Acta Chem Scand*, 6 (1952) 1485.
8 Price G J, *Ultrasonic Sonochem*, 3 (1996) 5229.
9 Algeria A & Lian Y, *J Phys Chem*, 93 (1989) 4908.
10 Singh S, Praveen S, Shukla D, Yasmin M, Gupta M & Shukla J P, *J. Solution Chem*, 40 (2011) 889.
11 Pradhan S K, Dash S K, Moharana L & Swain B B, *Indian J pure Appl Phys*, 50 (2012) 161.
12 Palani R & Balakrishna S, *Indian J pure Appl Phys*, 48 (2010) 644.
13 Syal V K, Chauhan S & Gautam R, *Ultrasonics*, 36 (1998) 619.
14 Gupta V K, Singh A K, Bhardwaj S & Bandi K R, *Sensor Actuat B*, 197 (2014) 264.
15 Pegu R, Mandal R, Guha A K & Pratihar S, *New J Chem*, 39 (2015) 5984.
16 Zhang E, Ju P, Zhang Z, Yang H, Tang L, Hou X, You J & Wang J J, *Spectrochim Acta A*, 222 (2019) 117207.
17 Abdelhedi M, Jabbar R, Mnif T & Abbes C, *Arab J Geosci*, 13 (2020) 180.
18 Thete R, Sharma S & Rajagopalan S, *AIP Conference Proceedings*, 2220 (2020) 140052.
19 Nath G, Tripathy A & Paikaray R, *Int J Thermophys*, 11 (2013) 2160.
20 Nath G, *Chem Sci Trans*, 3 (2012) 516.
21 Sharma P, Chauhan S, Chauhan M S & Syal V K, *Indian J pure Appl Phys*, 46 (2008) 839.
22 Vamsikrishna N, Kumar M P, Ramesh G, Ganji N & Daravath S, *J Chem Sci*, 129 (2017) 609.
23 Westcott A, Sumby C J, Walshaw R D & Hardie M J, *New J Chem*, 33 (2009) 902.