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## ACOUSTICAL STUDY OF EFFECT OF TEMPERATURE ON SYNTHESIZED ISONIAZIDE SCHIFF BASES IN ETHANOL SOLVENT BY USING INTERFEROMETER

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### ABSTRACT:

The ultrasonic velocity and density of synthesized isoniazide Schiff bases of 4-pyridine carboxylic acid, (2E)-2[(2-hydroxy 5-methoxyphenyl) methylene] hydrazide (HMB-INH) and 4-pyridine carboxylic acid (E)-N'-((2-hydroxynaphthalen-1-yl) methylene) isonicotinohydrazide (HNM-INH) in ethanol solvent at different temperature as 303.15 to 318.15K are analyzed by using interferometer. Obtained data are used to evaluate the various acoustical parameters such as intermolecular free length (Lf), Partial molal volume ( $\Delta v$ ), and adiabatic compressibility ( $\Delta s$ ), Solvation number (Sn), Relative association (RA) specific acoustic impedance (Z), apparent molal compressibility ( $\Delta k$ ).

**KEYWORDS:** Interferometry, Schiff bases, HMB-INH, HNM-INH, Acoustical parameter.

### Article History

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### INTRODUCTION:

In the Interferometrically has investigated aqueous and non-aqueous medium interaction between ions of solute and solvent. Many researchers have been studying the ultrasonic velocity in aqueous and non-aqueous electrolytic solution and they found to the nature of interaction between the solute and solvent in the solution.<sup>1-7</sup> Interferometric technique is a vital role in the determination of ultrasonic properties of solution and its measure the densities, ultrasonic velocity and intermolecular free length of the solution. The frequency of waves greater than 20 KHz are known as ultrasonic waves. The ultrasonic velocity has been successfully used to the determination of liquid metal channel flows.<sup>8</sup> Ultrasonic techniques could be applied for the determinations of moisture content and texture parameters after prolong ripening.<sup>9</sup> The measurements of ultrasonic waves are applicable in the study of molecular interactions in liquids solution, which gives valuable information regarding about complex formation, internal pressure, internal structure and molecular association.<sup>10</sup> The ultrasonic

parameters are directly related to the thermodynamic Parameters. Since various molecular theories of liquid state are based on the thermodynamic consideration, ultrasonic absorption study and velocity determination provides means to study them.

Literature review of Patil and Manusmare<sup>11</sup> have been reported the aqueous Sodium-Propionate molecule at Different Temperatures and it was observed the value of the density( $\rho$ ),viscosity( $\eta$ ) and ultrasonic velocity ( $u$ ) of aqueous solution of sodium propionate of binary liquid mixtures (0.01 to 1.0) mol.kg<sup>-1</sup> have been measured at different temperature range (298.15,303.15,308.15) K. Saini and its co-workers<sup>12</sup> have founded thermodynamic and thermo physical parameters of aqueous choline chloride solution with electrolyte solution such as zinc sulphate, potassium chloride and sodium chloride solution.They has been showing solute solvent interaction and structural effect on the solvent in the solution at different temperature. Many researchers are also investigating the ultrasonic parameters such as ultrasonic velocity, density and also of ternary organic mixtures at different temperature.<sup>13</sup> it has evaluated the strong molecular interaction between them. Pankaj and Bhatt<sup>14</sup> were investigating the acoustical properties of polyvinyl acetate at 0.50-2.00% concentration range at different temperature 35<sup>o</sup> to 55<sup>o</sup> C and they observed that density decreases with the increase in temperature and also ultrasonic velocity decreases. An increase in the ultrasonic velocity with an increase in the concentration and it appears to be associated with an overall increase in the cohesion in the said system.

#### **EXPERIMENTAL:**

The ligand of isoniazide Schiff bases was synthesis according to literature process by known technique. The one pot synthesis are carried out for ligands of isoniazide schiff bases as 4-pyridine carboxylic acid, (2E)-2[(2-hydroxy 5-methoxyphenyl) methylene] hydrazide (HMB-INH) and 4-pyridine carboxylic acid (E)-N'-((2-hydroxynaphthalen-1-yl) methylene) isonicotinohydrazide (HNM-INH) and it had purified by Vogel's method<sup>9</sup>. The Purified synthesized INH-Schiff bases are used and also used all the analytical grade (AR) chemicals. The purified ethanol was used the different concentrations of INH-Schiff ligands solutions were prepared by dissolving appropriate amount of solute in ethanol- solvent. The density of pure solvent and solutions were measured by specific gravity bottle having 10 mL capacity relative measurement method with accuracy  $\pm 1 \times 10^{-5}$  gm/cm<sup>3</sup>. The ultrasonic velocity was measure by using ultrasonic interferometer having frequency 3MHz (Model No.F-81). The various temperatures are maintaining by circulating water through the double wall measuring cell made up of steel and temperature had changed by using digital thermostate. In this analysis, the different ultrasonic properties are investigated such as specific acoustic impedance, apparent molal compressibility, apparent molal volume, relative association, intermolecular free length, adiabatic compressibility, solvation number, apparent molal compressibility, limiting apparent molal volume, and solvation number constant ( $S_k$ ,  $S_v$ ) have been evaluated

#### **RESULTS AND DISCUSSION:**

The obtained data of density and ultrasonic velocity are used to investigate the acoustical parameters and related mentioned in the given table 1-3 at 303.15 to 318.15K temperatures. From this statistical information, It has concluded that when the temperature is increases from 303.15 to 318.15 K of different solute of Synthesized INH-Schiff bases molecules in ethanol solvent then decreased density of all solution that time also increases the ultrasonic velocity of all solutions. It means that the ultrasonic velocity is employing the relation with intermolecular free length. The variation of ultrasonic velocity in solution depends upon the increase or decrease

of intermolecular free length after increasing the temperature from 303.15 to 318.15 K then sound was generated. From the values of ultrasonic velocity, it is apparent that a definite structural re-adjustment of molecular packing is taking place in solution. The increase in sound velocity is a consequence of the enhanced bulk modulus of the liquid mixture over and above its value for ideal mixing condition.<sup>14</sup>

Table no.2 shows the variation of adiabatic compressibility with temperature. It is observed from table no.2 that adiabatic compressibility decreases with increase in temperature but, the decrease in adiabatic compressibility indicates the enhancement of the bond strength at this concentration and also seen that acoustic impedance decreases with increase in temperature. This is in agreement with requirement as both ultrasonic velocity and density increase with increase in temperature of solution. So, there was more effective due to solute-solvent interactions in the solution.

It is found that  $S_v$  positive value shows more closer solute-solvent interaction in between synthesize schiff bases and ethanol solvent for all system in the table no-3. Solute-solvent also affect on apparent molal volume due to interaction very close vicinity in between solute and solvent i.e. these interaction increases then increases apparent molal volume with increasing value of apparent molal compressibility. In other words it shows weak electrostatic force of attraction between the close vicinity of ions.

Table-1 Temperature, density, ultrasonic velocity, adiabatic compressibility ( $\beta_s$ ), Specific acoustic impedance (Z) Intermolecular free length ( $L_f$ ).

4-pyridine carboxylic acid, (2E)-2[(2-hydroxy 5-methoxyphenyl) methylene] hydrazide (HMB-INH)					
Different temperature	Density (ds) Kg m <sup>-3</sup>	Ultrasonic velocity (Us) m s <sup>-1</sup>	Adiabatic compressibility $\beta_s \times 10^{-10}$ m <sup>2</sup> N <sup>-1</sup>	Inter molecular free length ( $L_f$ ) x 10 <sup>-11</sup> m	Specific acoustic impedance (Zx10 <sup>6</sup> ) kg m <sup>-2</sup> s <sup>-1</sup>
303.15	827.50	1567.97	4.9151	4.4589	1.2975
308.15	820.10	1575.16	4.9155	4.4591	1.2917
313.15	809.50	1591.11	4.8802	4.4430	1.2879
318.15	803.40	1611.04	4.7959	4.4045	1.2843
4-pyridine carboxylic acid (E)-N'-((2-hydroxynaphthalen-1-yl) methylene) isonicotinohydrazide (HNM-INH)					
303.15	831.00	1571.23	4.8758	4.4410	1.3355
308.15	823.60	1621.00	4.6208	4.3283	1.3351

313.15	811.41	1632.10	4.6272	4.3263	1.3242
318.15	806.62	1642.10	4.5982	4.3128	1.3237

**Table-2** Concentration (m), Relative association ( $R_A$ ), apparent molal compressibility ( $\beta_k$ ), apparent molal volume ( $V_v$ ), Solvation number ( $S_n$ )

4-pyridine carboxylic acid, (2E)-2[(2-hydroxy 5-methoxyphenyl) methylene] hydrazide (HMB-INH)				
Different temperature	Apparent molal volume ( $V_v$ ) $m^3mole^{-1}$	Apparent molal compressibility ( $\beta_k \times 10^4$ ) $m^2N^{-1}$	Relative association ( $R_A$ )	Solvation number ( $S_n$ )
303.15	0.3277	1.6094	1.0082	0.9182
308.15	0.3307	1.6241	1.0054	0.9218
313.15	0.3350	1.6335	0.9962	0.9217
318.15	0.3376	1.6170	0.9922	0.0790

4-pyridine carboxylic acid (E)-N'-((2-hydroxynaphthalen-1-yl) methylene) isonicotinohydrazide (HNM-INH)				
Different temperature	Apparent molal volume ( $V_v$ ) $m^3mole^{-1}$	Apparent molal compressibility ( $\beta_k \times 10^4$ ) $m^2N^{-1}$	Relative association ( $R_A$ )	Solvation number ( $S_n$ )
303.15	0.3504	1.7071	1.0114	0.9070
308.15	0.3535	1.6313	0.9953	0.8622
313.15	0.3589	1.6583	0.9859	0.8714
318.15	0.3610	1.6575	0.9867	0.0765

**Table-3** Limiting Apparent molal compressibility ( $\phi^k$ ), Limiting Apparent molal volume ( $\phi^v$ ),  $S_v$  and  $S_k$

Ligands of INH-Schiff bases	Limiting Apparent molal volume ( $\phi^v$ ) $\text{m}^3\text{mole}^{-1}$	Limiting Apparent molal compressibility ( $\phi^k$ ) $\times 10^{-10}$ $\text{m}^2\text{N}^{-1}$	$S_v$ $\text{M}^3\text{kg}^{-1/2}$ $\text{Mole}^{-3/2}$	$S_k$ $\text{M}^3\text{mole}^{-2}$ $\text{kg.Pa}^{-1}$
HMB-INH	0.1210	1.4090	0.0009	0.001
HNM-INH	0.1248	2.4093	0.0011	0.002

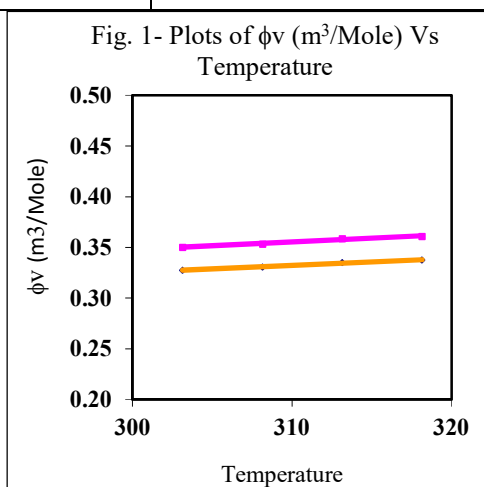


Fig.-1 -Apparent molal volume ( $\text{m}^3\text{mole}^{-1}$ )

Vs Concentration ( $\text{mole lit}^{-1}$ )

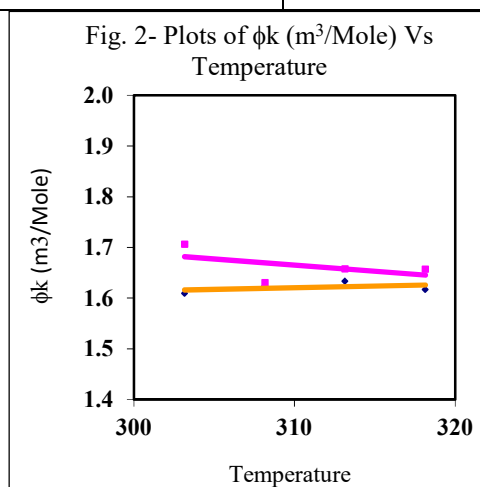


Fig.-2- Apparent molar compressibility  $10^{-9}(\text{m}^2\text{N}^{-1})$

Vs Concentration ( $\text{mole lit}^{-1}$ )

### CONCLUSION:

In present analysis the ultrasonic properties were determined from experimental information, it proves that there is interaction between Solvent and INH-Schiff bases ligands of HMB-INH and HNM-INH. From the data, we were concluded that there are weak molecular association was identified in INH-Schiff bases molecules. When temperature increases from top to bottom in the table no-2, then decreases the value of relative association, solvation number and value of  $S_k$  due to weak interaction between solvent- solute and it shows the strong coordination bond forms by solvent molecule in primary layer and here we are found decrease in size of secondary layer of Solvation.

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**REFERENCES:**

1. Mehra K. N. Tandon K. and Rawat M. K., (1991) *Acoustica*, 75, 15.
2. Khatun R., Sultana R., Ranjit N., (2018) *Orient J.Chem.* 34(4), 1755-1764.
3. Sharma S.K., Nathan V., Kumar D., Kishore K., (2017) *J.Mol.Liq. Volume*, 231, 647-654.
4. Pradhan S., Mishra S., (2019) *J.Mol.Liq*, 279(1), 561-570.
5. Mehra K. N., Chauhan M. and Shukla R. K., (1990) *Phys. Chem. Liq.*, 21, 239.
6. Nikam P. S. and Hiray A. R., (1991) *Indian J. Pure and Appl. Phys.*, 29, 601.
7. Rao M. G. S., (1971) *Indian J. Pure appl, Phys.*, 9, 169.
8. Bodke P. S., Binani S. S. and Joat R. V., (2014) *International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering*, 8(9), 993-996.
9. Andreev O., Kolesnikov Y. and Andrethess, (2009) *Exp.Fluid*, Vol.46, 77.
10. Liull P., Simal S., Fermentia A., Benedito J. and Rassello C., (2002) *J.Food Eng.*, Vol.52 (4), 323.
11. Patil K.C. and Manusmare P., (2019) *Jouranal of Applicable Chemistry*, 8 (3), 1385-1393.
12. Saini A., Prabhune A., Mishra A.P. and Dey Ranjan, (2021) *J. of Mol. Liquids*, Vol.323.
13. Vanathi V.,Mullainathan S.,Nithiyathanam S.,Ramasamy V. and Pallaniappan L., (2019) *Heliyon*, Vol.5(8).
14. Singh P.K. and Bhatt S.C., (2010) *Applied Physics research*, Vol.2 (1), 35-45.

**SYNTHESIS, SPECTRAL STUDIES & BACTERIAL ACTIVITY OF SCHIFF BASE  
LIGAND DERIVED FROM 4-AMINOANTIPYRINE**

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**Abstract:-**

The Schiff bases ligand synthesised from the condensation of primary amines like 4-aminoantipyrine with 5-chloropyrazole - 4 - carbaldehyde.

The synthesized ligand characterized by techniques like TLC, MP, Solubility. Spectroscopic techniques like IR, NMR, CMR and Mass, also the antibacterial activity of the ligand were tested against some bacteria.

**Keywords:-** Schiff base ligand, spectra study.

**Introduction:-**

The Schiff bases are important class of organic compound (1). They were first reported by Hugo Schiff in 1864 (2). The azomethine group  $RCH=NR'$  present in Schiff bases ligand formed by condensation of primary amine & aldehyde (3). Where R & R' are alkyl, aryl, cyclo alkyl or heterocyclic group (1). The formation of Schiff bases generally takes place under acid or base catalysis or with heat.

The common Schiff bases are crystalline solids, Schiff bases are used as intermediates for the synthesis of amino acids or as ligands for the preparation of metal complexes having a series of different structures.

Heterocyclic compounds containing one or more hetero atoms have a wide range of applications in pharmaceuticals, agrochemicals, and veterinary products [4,5]. Schiff bases play an important role in their significant bio-activities and containing azomethine ( $-N=CH-$ ) as an active pharmacophore [6]. Schiff bases act as an important starting material for synthesis of new drug design and intermediate in organic syntheses, or rubber additives [7]. They have received **much more attention** in the field of biology and chemistry due to their chemotherapeutic value [8]. Schiff bases are synthesized by the condensation of primary amine with an aldehyde or a ketone used as amino protective groups in organic synthesis [9-11]. Metal ions can form complex with Schiff bases as a ligand and liquid crystals in analytical, medicinal, and polymer chemistry [12,13].

The Schiff base ligand containing O, N donor atoms acts as superior chelating agents for the transition and non-transition metal ions and showed remarkable biological activity [14,15]. Coordination of Schiff base ligand with transition metal ions such as copper, Cobalt often enhances their activities [16]. Many metal complexes show powerful antimicrobial activities in medicinal field [17]. Thus inorganic elements play crucial roles in biomedical and biological processes. Many drugs possess modified toxicological and pharmacological properties in the form of metal complexes [18]. The incorporation of metal ion in the form of complex showing some degree of antibacterial [19], antifungal [20], antitumor [21], and anti-inflammatory activity [22,23]. Metal complexes of Schiff base ligand derived from heterocyclic compounds have increased interest in the field of bioinorganic chemistry. The coordinating property of 4-aminoantipyrine ligand has been modified to give a flexible ligand system formed by condensation with variety of reagents like aldehydes, ketones [24,25].

**Materials & Methods:-**

All the chemicals and solvent used were A.R grade and were obtained from Sigma-Aldrich. All the solvent were used without purification. FTIR spectra were registered on SHIMADZU infra red spectrophotometer using KBr discs. The  $^1H$ -NMR spectra of ligand was recorded in DMSO using Bruker Avance 400MHz NMR Spectrometer.

MP were recorded using open capillary method.

**Preparation of Ligand**

To a solution of 4-aminoantipyrine (0.1mol) and 5-chloro-3-methyl-1-phenyl-pyrazole-4-carbaldehyde (0.1mol) in 20 ml ethanol was added. A few drops of 10% NaOH were added to adjust the pH and the reaction mixture then refluxed with stirring for 2 hrs progress of reaction was monitored by TLC. After the completion of reaction the obtained product was collected by filtration through buchner funnel. Solid obtained was recrystallised from suitable solvent. (26-28). Physical characterisation of schiff base ligand are given in Table 1

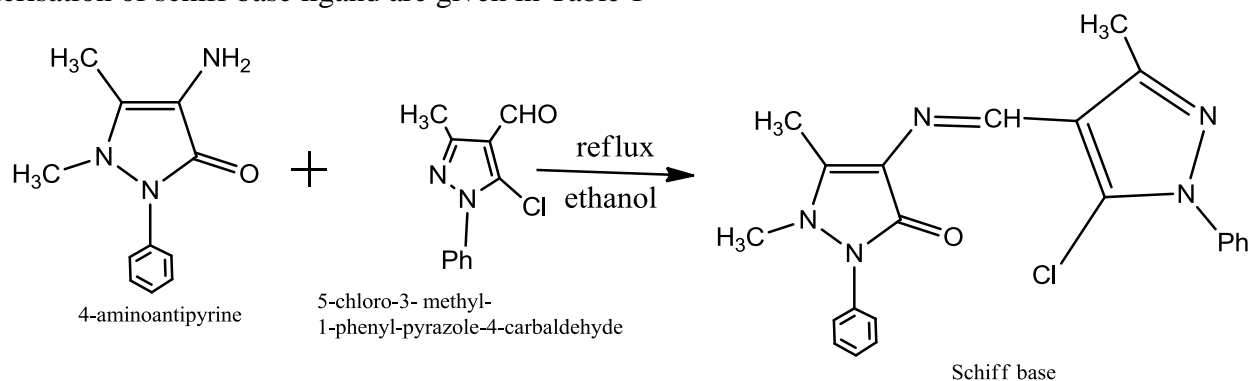


Table 1 Physical characterisation of the Schiff base

Comp	M.F.	Physical State	M.P.	Yield
L	C <sub>22</sub> H <sub>20</sub> N <sub>5</sub> OCl	yellow	284 <sup>0</sup> C-286 <sup>0</sup> C	86.2%

**Result and discussion:-**

The synthesis of schiff base using primary amine and aldehyde in ethanol as a solvent resulted in a schiff bases with general formula RCH=NR

The prepared ligand is yellow in colour and it is soluble in common organic solvent but insoluble in water as shown in Table 2

Table 2 Solubility of prepared schiff base ligand

Ligand	Acetone	Ethanol	Methanol	Hexane	Chloroform
L	S	S	S	S	S

Petrolleum ether	Ether	CHCl <sub>2</sub>	Benzene	DMF	DMSO	Water
S	S	S	S	S	S	IN

S = Solubility

IN = Insolubility

**Spectral characterisation:-****1) FT-IR data:-**

When the infrared light is passed through a sample of organic compound, some of the frequencies absorbed & the absorbed or the transmitted is plotted against frequency, the result is infrared spectrum. The excitation of molecular vibration & rotation gives rise to absorption in the infrared region of the spectrum. The ligand is stable & has sharp MP that indicate the purity of ligand. The IR data of ligand; IR (cm<sup>-1</sup>); 1612, -C=N

**2) <sup>1</sup>H-NMR Spectra of the ligand:-**

The <sup>1</sup>H-NMR spectra of ligand was recorded in DMSO using Bruker Avance 400MHz NMR Spectrometer & it showed a number of characteristics signals of the ligand

<sup>1</sup>H NMR (δ ppm); 9.5 (s, 1H, =CH); 7.61-7.47 (m, 7H); 7.39-7.34 (m, 3H); 3.1 (s, 3H, -N-CH<sub>3</sub>); 2.5 (s, 3H, =C-CH<sub>3</sub>); 2.09 (s, 3H, =C-CH<sub>3</sub>)

**3) <sup>13</sup>C-NMR Spectra:-** <sup>13</sup>C-NMR spectra of the Schiff base was recorded in DMSO-d<sub>6</sub> & are shown in fig. 1. <sup>13</sup>C-

NMR; (δ ppm); 159.68; (C=O); 151.78; (=CH); 148.77; 146.88; 137.33; 134.55; 129.00; 128.10; 128.26; 127.54; 126.59; 124.66; 124.33; 116.35; 117.25; 35.40; (-N-CH<sub>3</sub>); 14.57 (=C-CH<sub>3</sub>); 9.68 (=C-CH<sub>3</sub>)



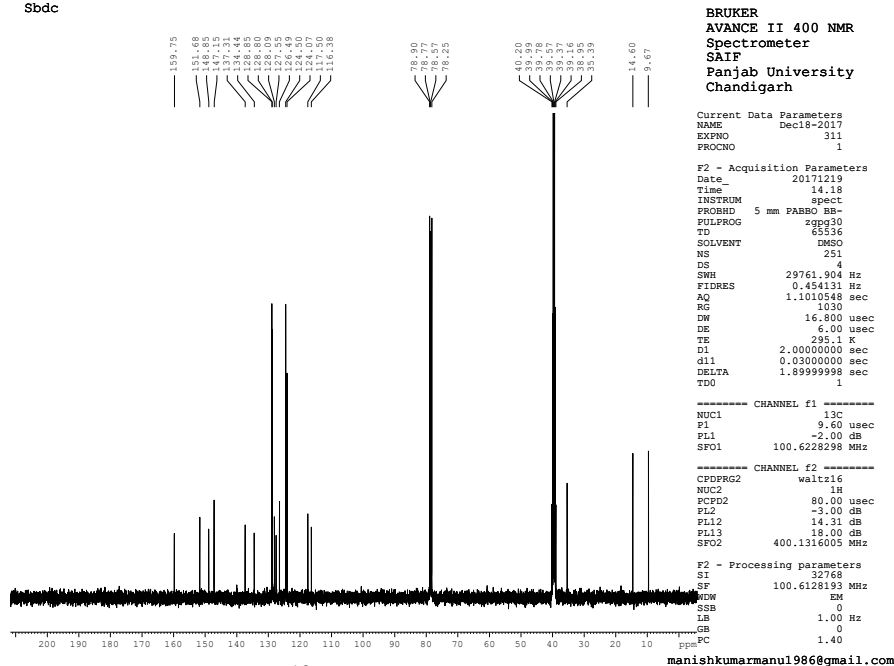


Fig.1 <sup>13</sup>C-NMR spectra of the ligand

4) Mass spectra:-

The formation of ligand was confirmed through MS technique. Fig 2 shows the mass spectrum of ligand. The molecular ion peak was observed at m/z=405(m+1) consistent with the molecular weight of ligand confirm the formation of ligand.

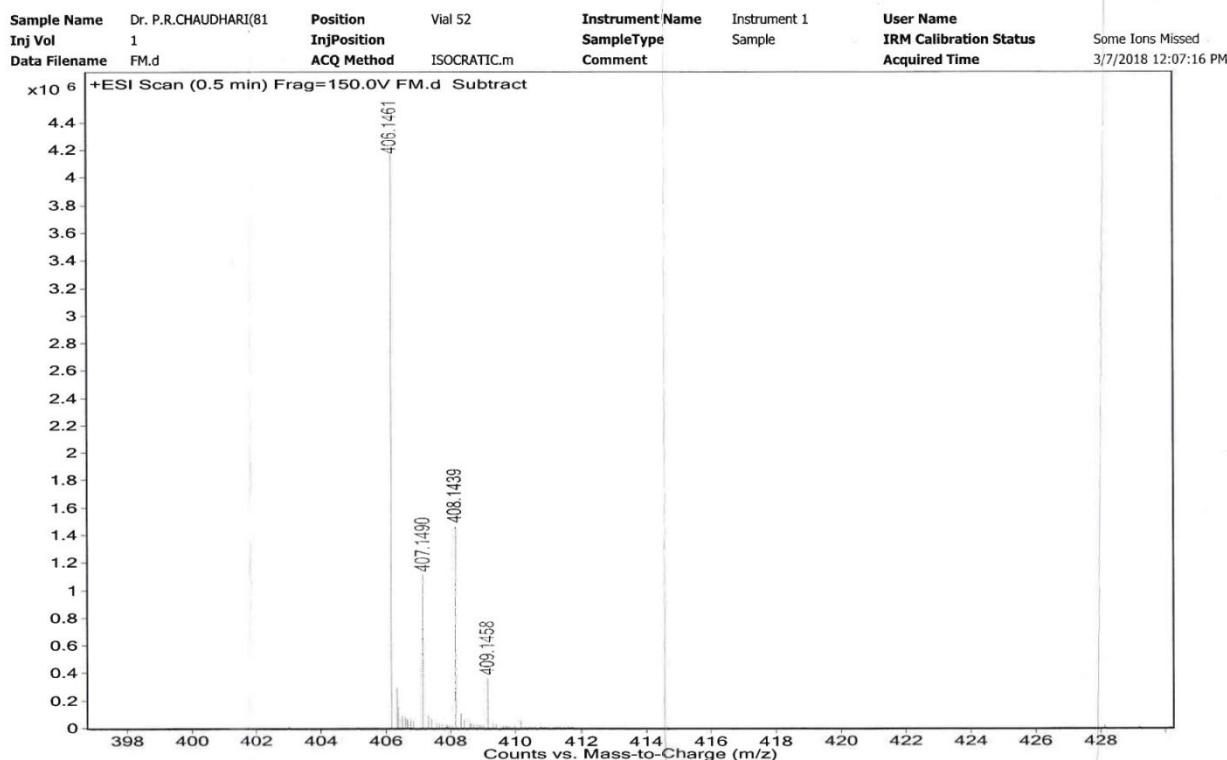


Fig.2. Mass spectrum of ligand

Biological activity studies:-

The antibacterial activity of the Schiff base ligand were tested against the some bacteria E-coli,(gram negative bacteria) & S-aureus(gram positive bacteria).

In a typical procedure molten nutrient agar kept at 115<sup>0</sup>C-120<sup>0</sup>C was poured into a petri dish & allowed to solidify. The small wells were made in the agar medium by carefully using a sterile cork & these were completely filled with test solution. The plates were incubated at 24 hrs at 37<sup>0</sup>C . The diameters of the zone of inhibition for the test compound were measured in millimeter.

The data of the antibacterial activity of ligand given in table 3.

Table 3 The bacterial activity data for Schiff base

comp	Inhibition zone diameter		
	E-coli	S-aureus	P-vulgarius
L	10mm	8mm	6mm

The results of antibacterial activity are shown in fig 3



Fig3 Result of antibacterial activity

#### Conclusion:-

The Schiff base ligand 4-((5-chloro-3-methyl-1-phenyl-pyrazol-4-yl)methyleneamino)-2,3-dimethyl-1-phenyl pyrazole-5-one has been synthesised as given in scheme 1 the structure of above ligand were in good agreement with spectral and analytical data.

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#### References:-

1. Aurlmuraqan, S, kavitha pH, venkatraman RP (2010) Biological activity of Schiff base and its complexes, a review rasayan J. Chem (3) 385-410.
2. Schiff H (1864) Mitteilungen aus dem universitatlaboratorium in pisa Ein neuer eihe organischer basen.
3. A.H.EL-masre, H.H.FaHmy and S.H.abdelwahed, molecules, 5, 1429 (2008)
4. Azab ME, Rizk SA, Amr AE-GE. Synthesis of some novel heterocyclic and schiff base derivatives as antimicrobial agents. Molecules 2015; 20(10):18201–18.
5. Brzezinska-Rodak M, Peczynska-Czoch W. Biodegradation of N-heterocyclic compound. Biotechnologia 2000; 1:102–16.
6. Kumar J, Rai A, Raj V. A comprehensive review on the pharmacological activity of schiff base containing derivatives. Org Med Chem J 2017; 1:555–64.
7. Brodowska K, Lodyga-Chruscinska E. Schiff bases—interesting range of applications in various fields of science. Chem Inform 2015; 46(11).
8. Ashraf MA, Mahmood K, Wajid A, Maah MJ, Yusoff I. Synthesis, characterization and biological activity of Schiff bases. IPCBEE 2011; 10:1–7.

9. Qin W, Long S, Panunzio M, Biondi S. Schiff bases: A short survey on an evergreen chemistry tool. *Molecules* 2013; 18(10):12264–89.
10. MOHAMED GG, Omar MM, Hindy AM. Metal complexes of Schiff bases: preparation, characterization, and biological activity. *Turkish Journal of Chemistry* 2006; 30(3):361–82.
11. Deshmukh P, Kumar P, Kankoriya A, Halve AK, Dixit R. 4-Aminoantipyrine: a significant tool for the synthesis of biologically active Schiff bases and metal complexes. *Int J Pharm Sci Rev Res* 2015; 34(1):162–70.
12. Prakash A, Adhikari D. Application of Schiff bases and their metal complexes-A Review. *Int J Chem Tech Res* 2011; 3(4):1891–6.
13. Ibrahim MN, Sharif SE. Synthesis, characterization and use of Schiff bases as fluorimetric analytical reagents. *Journal of Chemistry* 2007; 4(4):531–5.
14. kaushik N K. and Mishra A K, Synthesis, Characterization and thermal studies of some new organotin (IV) complexes with aniline N-thiohydrazide and benzaldehyde aniline N-thiohydrazone, *Indian Journal of Chemistry A*,42(11):2762-2766,(2003).
15. Saravia MS, Quinti S, Portugal FC Metal, Nitrogen donor ligands bearing N-Hgroups, effect on catalytic and cytotoxic activity of molybdenum<sup>3+</sup>-allyldicarbonyl complexes, *Journal of organometallic chemistry*, 693 (21-22): 3411-3418, (2008)
16. Singh NK, Srinivastava A, Sodhi A, and Ranjan P. In vitro and in vivo antitumor studies of a new thiosemicarbazide derivative and its complexes with 3D - metal ions, *Transition Metal Chemistry* 25 (2): 33 140, (2000)
17. Islam MN, Shahriar S MS, Islam MK, Jesmin M, Ali MM, Khanam JA, Antibacterial Activities of Some Transition Metal Schiff Base Complexes, *International Letters of Chemistry, Physics and Astronomy*, 5: 12-20, (2013).
18. Dhivya Priya D, Akila E, Usharani M, and Rajavel R, Synthesis, Spectral and Biological Activity of Mixed Ligand Schiff Base Complexes Derived From Salicylaldehyde, *International Journal of Pharmacy & Technology*, 4 (1): 4067 4078, (2012).
19. Kabeer AS, Baseer MA, Mote NA Synthesis and antimicrobial activity of some Schiff bases from Benzothiazoles *Asian. J. Chem.* 13 (2): 496-500, (2001).
20. Singh W M, Dash B C, Synthesis of some new Schiff bases containing thiazole and oxazole nuclei and their fungicidal activity, *Pesticides* 22 (11): 33–37. (1988).
21. Desai SB, Desai PB, Desai KR, Synthesis of Some Schiff Bases, Thiazolidinones And Azetidinones Derived From 2,6-Diaminobenzo[1,2-D:4,5-D']Bisthiazole And Their Anticancer Activities, *Heterocycl. Commun.* 7 (1): 83 90. (2001).
22. Zahid HC, Mohammad S I, Hummara SI, Claudiu TS, Transition Metal Acetylsalicylates and Their Anti Inflammatory Activity, *Journal of Enzyme Inhibition and Medicinal Chemistry* 17 (2): 87, (2002).
23. Parashar RK, Sharma RC, & Govind Mohan, Schiff bases derived from Salicylaldehyde and 2 - substituted aniline and their metal chelates with Cu (I), Ni (II), and Co(II) ions were synthesized and screened for the anti-inflammatory and antiulcer activity, *Biological Trace Element Research*, 145 (1989).
24. Suresh MS, & Prakash V, Preparation and characterization of Cr (III), Mn (II). Co(III), Ni (II), Cu (II). Zn (II) and Cd (II) chelates of schiffs base derived from vanillin and 4 - amino antipyrine, *J of the Physical Sciences*, 5 (14) 2203-2211, (2010).
25. Osole A, Synthesis and Characterization of Some Tetradentate Schiff - Base Complexes and Their Heteroleptic Analogues, *E - Journal of Chemistry*, 5 (1): 130-135, (2008).
26. Vogel practical organic chemistry Book (5), 1150
27. O.C.Okpareke, J.N.Asegbeloyin, E.C Okar, O.T.Ujamand, S.O.E.okereke, *Int.J.chem.sci*; 10 (4) 2012 1849-1858
28. K.Sparikh & S.P.Vyas *JCPR*, 4 (5) (2012) 2681-2683.

**INVESTIGATION OF ULTRASONIC PARAMETERS SYNTHESIZED SCHIFF BASE OF N (2-HYDROXY-5-METHOXYBEZYLIDENE ISONICOTINOHYDRAZIDE IN ETHANOL SOLVENT AT 303<sup>o</sup>K.**

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**ABSTRACT:-**

By using the interferometer to investigating the ultrasonic velocity and density data of Schiff base N(2-Hydroxy-5-methoxy benzylidene)isonicotinohydrazide the ultrasonic parameters have been studied in ethanol solvent at 303K. The ultrasonic parameter such as intermolecular free length (Lf), adiabatic compressibility ( $\beta_s$ ), Partial molal volume ( $\beta_v$ ), specific acoustic impedance (Z), apparent molal compressibility ( $\beta_k$ ), relative association (RA), solvation number (Sn) have been evaluated and from the obtained data it is clear that solute of N(2-Hydroxy-5-methoxy benzylidene)isonicotinohydrazide having more interaction with ethanol solvent.

**KEY WORD:** - Schiff base of N (2-Hydroxy-5-methoxy benzylidene) isonicotinohydrazide  
Densities of solution, Ultrasonic velocity Apparent molal volume, Adiabatic compressibility.

**INTRODUCTION:-**

In the recent year many researchers have been discovered such as ultrasonic velocity, solute-solvent, ion-solvent interaction in non-aqueous [1-5]. Jahagirdar & its co-workers determined ultrasonic properties of various complexes in methanol solvent [6]. Kachare & its coworkers concluded that, solute solvent interaction of various shapes and size of the compounds [7]. Kawaizumi F. & its coworkers have been discovered acoustical properties of complex in water [8]. Bhatt & its coworkers have been investigated ultrasonic characteristics of sodium salt of N- chloro-p-toluene sulphonamide in aqueous binary mixture system [9]. The acoustical properties of 2-(hydroxy-5-bromophenyl)-3-(4-chloro phenyl)1,3-pronandione in various percentage of dioxane-water mixture were studied by Thakur & its coworkers[10]. Meshram & its coworkers found the different acoustical properties of some substituted Pyrazolines in acetone-water binary mixture[11]. And they concluded the ultrasonic velocity different with different concentration. Many literature articles showed ultrasonic velocity of liquid mixture was more beneficially in the understanding nature of molecular interaction [12-19]. And physicochemical characteristics of liquid mixture [20-21]. Palani & its coworkers also discovered the ultrasonic velocity and density of amino acid in aqueous solution of magnesium acetate at constant temperature[22]. Tadmalkar and its co workers were determined the thermodynamic and acoustical properties of citric acid in water at different temperatures[23]. Mishra & its coworkers have been evaluated ultrasonic of properties such as ultrasonic velocity and density of metal complex in non-aqueous solution [24]. Many researchers have been defined thermodynamic parameters and acoustic properties for the solution of amide and amines in benzene, Water, 1-propanol binary mixture and the molecular interaction of liquids [25-26].

**EXPERIMENTAL SECTION:-**

After literature review we were interest in the study of ultrasonic's properties of synthesized Schiff base of N (2-Hydroxy-5-methoxy benzylidene) isonicotinohydrazide. The frequency 3MHz ultrasonic interferometer was used to determine the ultrasonic velocities. The maintained constant temperature by circulating water in the double steel cell wall measuring. The solution of different concentration of Schiff base was prepared in ethanol solvent. For the measuring densities of different solution and solvent by using the specific gravity bottle having accuracy  $\pm 1 \times 10^{-5}$  gm/cm<sup>3</sup>.

In the present work we have been determined different densities and different properties such as relative association (RA), intermolecular free length (Lf), adiabatic compressibility ( $\beta_s$ ), limiting apparent molal volume( $\beta_v^{\infty}$ ), apparent molal volume ( $\beta_v$ ), apparent molal compressibility

( $\beta_s$ ), specific acoustic impedance (Z), limiting apparent molal compressibility( $\beta_k$ ), solvation-number( $S_n$ ) and constant ( $S_k$  &  $S_v$ ). The sound velocity of Schiff base N (2-Hydroxy-5-methoxy benzylidene) isonicotinohydrazide have been measured in the various concentration range as given in the below

**THEORY AND CALCULATION:-**

The ultrasonic velocity is calculated by using relation, Ultrasonic velocity (U)

$$U = \lambda \times \text{Frequency} \times 10^3 \text{----- (1)}$$

some ultrasonic parameters have been calculated using the standard relations.

Adiabatic compressibility solution ( $\beta_s$ ) =  $1 / U_s^2 \times d_s$ ----- (2)

Adiabatic compressibility solvent ( $\beta_0$ ) =  $1 / U_0^2 \times d_0$ ----- (3)

Apparent molal compressibility ( $\beta_k$ ) is determine by using the relation

$$(\beta_k) = 1000 \times \left( \frac{d_0 - d_s}{m \times d_s \times d_0} \right) + \frac{\beta_s d_0 - \beta_0 d_s}{d_s} \text{----- (4)}$$

Where  $d_s, \beta_s$  and  $d_0, \beta_0$  are the density and adiabatic compressibility of solution and solvent respectively. m is concentration of solute in terms of molality and The molecular weight of solute is M.

Apparent molal Volume ( $\phi_v$ ) has been calculated by using the relation,

$$(\phi_v) = \frac{M}{d_s} \times \frac{(d_0 - d_s) \times 1000}{m \times d_s \times d_0} \text{----- (5)}$$

Specific acoustic impedance (Z) =  $U_s d_s$

Intermolecular free length ( $L_f$ ) =  $K \sqrt{\beta_s}$

Relative association ( $R_A$ ) =  $(d_s / d_0) \times (U_0 / U_s)^{1/3}$  ----- (6)

$$\beta_k = \beta_0 + S_k C \text{----- (7)}$$

$$\phi_v = \phi_v^0 + S_v C \text{----- (8)}$$

**Table-1 Density (ds), Ultrasonic velocity (Us), adiabatic compressibility ( $\beta_s$ ), Specific acoustic impedance (Z) and Intermolecular free length ( $L_f$ ).**

**Schiff base of N (2-Hydroxy-5-methoxy benzylidene) isonicotinohydrazide in ethanol:**

Concentration moles lit <sup>-1</sup> (m)	Density (ds) Kg.m <sup>-3</sup>	Ultrasonic velocity (Us) m.s <sup>-1</sup>	Adiabatic compressibility ( $\beta_s$ )x10 <sup>-10</sup> m <sup>2</sup> N <sup>-1</sup>	Intermolecular free length ( $L_f$ )x10 <sup>-11</sup> m	Specific acoustic impedance (Zx10 <sup>6</sup> ) kg m <sup>-2</sup> .s <sup>-1</sup>
1x10 <sup>-3</sup>	792.68	1579	5.05985	4.524	1.2516
2x10 <sup>-3</sup>	792.71	1589	4.99618	4.4955	1.2596
3x10 <sup>-3</sup>	792.75	1598	4.93981	4.4700	1.2668
4x10 <sup>-3</sup>	792.77	1607	4.88451	4.4450	1.2740
5x10 <sup>-3</sup>	792.79	1613	4.84812	4.4284	1.2788
6x10 <sup>-3</sup>	792.82	1635	4.71835	4.3687	1.2963
7x10 <sup>-3</sup>	792.85	1649	4.63839	4.3315	1.3074
8x10 <sup>-3</sup>	792.86	1657	4.59366	4.3106	1.3138
9x10 <sup>-3</sup>	792.87	1662	4.56601	4.2976	1.3177

**Table-2 Concentration (m), Solvation number (S<sub>n</sub>), Relative association (R<sub>A</sub>), Apparent molal volume ( $\phi_v$ ), Apparent molal compressibility ( $\beta_k$ ).**

Concentration (m) Moles.lit <sup>-1</sup>	Apparent molal volume ( $\phi_v$ ) m <sup>3</sup> mole <sup>-1</sup>	Apparent molar compressibility ( $\beta_k$ )x10 <sup>-10</sup> m <sup>2</sup> N <sup>-1</sup>	Relative association (R <sub>A</sub> )	Solvation number (S <sub>n</sub> )
1x10 <sup>-3</sup>	0.151211	1.73202	0.98988	1.002262

$2 \times 10^{-3}$	0.22283	1.70953	0.98656	0.9894441
$3 \times 10^{-3}$	0.241388	1.69586	0.98383	0.978074
$4 \times 10^{-3}$	0.258624	1.67102	0.98110	0.966948
$5 \times 10^{-3}$	0.268962	1.65804	0.97930	0.959618
$6 \times 10^{-3}$	0.273195	1.61308	0.97272	0.933532
$7 \times 10^{-3}$	0.276216	1.58501	0.96862	0.917448
$8 \times 10^{-3}$	0.282465	1.57085	0.96629	0.908457
$9 \times 10^{-3}$	0.287324	1.56283	0.96485	0.902893

### RESULTS AND DISCUSSION:-

From the experimental analysis the synthesized Schiff base of N (2-Hydroxy-5-methoxy benzylidene) isonicotinohydrazide obtained data density and ultrasonic velocity we had used to determined various ultrasonic's properties such as adiabatic compressibility ( $\beta_s$ ), Specific acoustic impedance (Z) and Intermolecular free length ( $L_f$ ) are recorded in table-1. Solvation number ( $S_n$ ), Relative association ( $R_A$ ), apparent molal volume ( $\Delta v$ ), apparent molal compressibility ( $\Delta \beta$ ) are recorded in table-2. Limiting Apparent molal compressibility ( $\Delta \beta_\infty$ ), Limiting Apparent molal volume and their constant ( $S_k$ ,  $S_v$ ) are recorded in table-3. It was investigated that when concentration for system increases from top to bottom the ultrasonic then velocity also increases (Table-1). And also decreases Intermolecular free length ( $L_f$ ) with impedance (Z) increased It was showed that The evidence for strong interaction between ions in solution is also due to apparent molal volume increase as the concentration increases. When increasing the concentration of synthesized schiff base of an electrolyte then increasing ionic strength This is clearly indicate that stronger force of attraction between solute and solvent. And this interaction weak hydrogen bonding so adiabatic compressibility is decreases due to weak force of attraction among them.

The table no.3 is clearly indicate that  $S_v$  value is positive and this  $S_v$  positive value shows more closer solute solvent interaction in between synthesize schiff base of N (2-Hydroxy-5-methoxy benzylidene) isonicotinohydrazide and ethanol solvent. Solute solvent also affect on apparent molal volume due to interaction very close vicinity in between solute and solvent i.e. these interaction increases then increases apparent molal volume with increasing value of apparent molal compressibility. In other words It shows weak electrostatic force of attraction between the close vicinity of ions. From the data, we were concluded that there are weak molecular association was identified in Schiff base of N (2-Hydroxy-5-methoxy benzylidene) isonicotinohydrazide. When concentration increases from top to bottom in the above table then decreases the value of relative association, solvation number and negative value of  $S_k$  due to weak interaction between solvent-solute and it shows the strong coordination bond forms by solvent molecule in primary layer. And here we are found decrease in size of secondary layer of Solvation.

**Table-3** Limiting Apparent molal compressibility ( $\Delta \beta_\infty$ ), Limiting Apparent molal volume ( $\Delta v_\infty$ ),  $S_v$  and  $S_k$

Ligand	Limiting Apparent molal volume ( $\Delta v_\infty$ ) $m^3 \text{mole}^{-1}$	Limiting Apparent molal compressibility ( $\Delta \beta_\infty$ ) $\times 10^{-10} m^2 N^{-1}$	$S_v$ $m^3 \text{kg}^{1/2} \text{mole}^{-3/2}$	$S_k$ $m^3 \text{mole}^{-2} \text{kg} \cdot N^{-1}$
Schiff base of N (2-Hydroxy-5-methoxy benzylidene) isonicotinohydrazide	0.184	1.758	13.46	-2.29



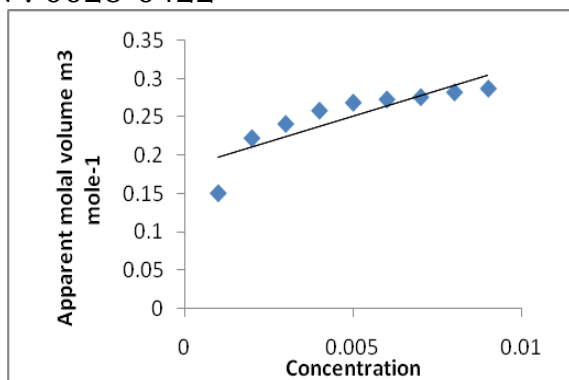


Fig-1 -Apparent molal volume (m<sup>3</sup>.mole<sup>-1</sup>) Vs Concentration (mole.lit<sup>-1</sup>)

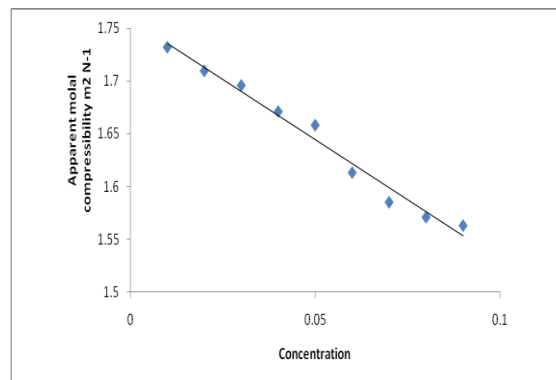


Fig-2- Apparent molar compressibility 10<sup>-10</sup> Vs Concentration (mole.lit<sup>-1</sup>)

## CONCLUSION:-

An experimental analysis data of density & ultrasonic velocity have been measured for Schiff base N (2-Hydroxy-5-methoxy benzylidene) isonicotinohydrazide in ethanol solvent at 303K. The ultrasonic parameters were calculated from analysis data. The presence of molecular type of interaction between solute-solute or ion-ion and solvent-solute exists between Schiff base of N (2-Hydroxy-5-methoxy benzylidene) isonicotinohydrazide were also studied with the help of experimental data. And finally concluded that from the experimental analysis the interaction between solute and solvent in Schiff base of N (2-Hydroxy-5-methoxy benzylidene) isonicotinohydrazide & ethanol systems are strong.

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## REFERENCES

1. A.Ali. and A.K.Nain, *Acoustics Lett.*, 19, 53(1996).
2. M.K.Rawat and Sangeeta, *Ind.J.pure Appl.Phy.*, 46,187-192(2008).
3. S.Baluja and S.Oza, *Fluid phases Equilibria.* 200(1), 49-54(2005).
4. H.Ogawa and S.J.Murakami, *J.Solution.Chem.* 16,315(1987).
5. D.Ubagaramary, Dr.P.Neeraja, *Journal of Applied Chemistry*, 2(5),01-19 (2012)
6. D.V.Jahagirdar, B.R.Arbad, S.R.Mirgane, and A.G.Shankarvar, *J.Molecular Liq.*, 33-43(1998).
7. A.V.Kachare, D.D.Patil, S.R.Patil, and A.N.Sonar, *Journal of Applicable Chemistry*, 2(5),1207-1215(2013).
8. F.Kawaizumi, K.Matsumoto and H.Nomura, *J.Phys.Chem.* 87(16), 3161-3166(1983).
9. J. I. Bhatt and N. V. Sabatha, *Ind. J. Chem.*, Vol.42A,520 (2003)
10. A. Solanki and I. Thakur *Indian Journal of Chemistry*, 45B, (2007)
11. Y.K.Meshram and M.L.Narwade, *Acta Ciencia Indica*, 27(2), 67-70(2001).
12. L. R. Lagemann and W. S. N. Dunbar, *J. Phys. Chem.*, 49(1995).
13. A. Wissler, *J. Amer Chem. Soc.*, 71, 1272(1949).
14. S. S. Aswale, P. B. Raghuvanshi, D. T. Tayade and S. R. Aswale, *J. Indian Chem. Soc.*, 84,159(2007).
15. J. D. Pandey, R. D. Rai, A. K. Shukla and N. Mishra, *Indian J Pure Appl Phys.*,31,84(1993).
16. Uvarani and J. Sivapragasam, *J. Chem. Pharm. Res.*, 4(1), 653-655(2012).
17. S. Velmourougane, T. K. Nambinarayanan, S. A. Rao and B. Krishnan, *Indian J.Phys.* 61B,105-110(1987).
18. D. Gomez- Diaz and J. M. Navaza, *J. Chem. Eng. Data*, 51,722(2006).
19. B. Gonzalez, A. Dominguez and T. Jojo, *J. Chem. Thermodyn.*, 36,267(2004).
20. J. D. Pandey and A. K. Shukla, *J. Pure Appl. ultroson*, 15,37(1982).
21. S. J. Bhatti, J. S. Vivk and D. P. Sing, *Acoustica (Germany)*, 50,291(1982).
22. A.Nithya, S. Nithyanandhan, S.Mullainthan and M.Rajasekaran, *E-Journal of Chemistry*, 6(1), 138(2009).
23. R.Palani and S.Saravanan, *Research J.Phy.* 2(1), 13-21(2008).
24. A.P.Mishra and D.K.Mishra, *J.Chemical. Pharm.Res.* 3(3), 489(2011).
25. M.Arvinthraj, S.Venktesan and D.Meera, *J.Chemical. Pharm.Res.* 3(2), 623(2011).
26. S.K. Thakur and S.Chauhan, *J.Chemical. Pharm.Res.* Vol.3 (2), 657(2011).
27. S.A.Mirrikar, P.P.Pawar, G.K.Bichile, *American Journal of Pharmacology and Pharmacotherapeutics*, 2(1), 2-7(2015).

# Studies on nanocomposites nanoplates and perovskite nanorod thin films

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## **Abstract:**

*Nano crystalline nickel oxide thin films of different film thickness were deposited onto glass substrate at 350 oC by varying volume of precursor solution using spray pyrolysis technique. This structural, morphological and microstructure properties were investigated using XRD, FE-SEM and TEM. The element composition was studied using EDAX. It is found that increase in the volume of sprayed solution leads to the increment in film thickness and amelioration of crystallinity of the film. The results are discussed and interpreted.*

**Keywords:** *Spray Pyrolysis, Nano crystalline nickel oxide, thin films, Electrical conductivity.*

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## **1. Introduction**

Semiconductor metal oxide, nanocomposites, perovskite thin films sensor is extensively used across several domains that involve gas analysis, including air quality monitoring, environmental pollution detection, and identification of harmful gases [1-3].

Recently, a lot of investigators have focused their attention towards studying gas sensing potential of NiO owing to its high thermal stability and unique nanostructure [4]. The gas sensing performance of conventional NiO sensors, however, are limited, including low sensitivity, weak reliability, and high operating temperature, which restricts the production of sensors with a high performance [5]. Additional challenges are posed by the hazardous effects of prolonged NO<sub>2</sub> exposure [6].

Owing to the chemical stability, SnO<sub>2</sub>, an *n*-type oxygen-deficient metal oxide, is most widely used for the fabrication of gas sensing sensors [7, 8]. Furthermore, the small size effect of SnO<sub>2</sub> makes it viable for the formation of n-n or p-n heterojunctions in conjunction with other nanomaterials [9].



Previous studies have shown that sensors made from NiO–SnO<sub>2</sub> nanocomposite combine the properties of both components and exhibit much better gas-sensing performances, lower optimum working temperature, rapid response-recovery, and better gas response than conventional SnO<sub>2</sub>-based sensors [10].

Several studies have been conducted to overcome the limitations of the conventional nanomaterials, such as alterations in morphology, doping with metals, nanocomposites, etc. [10-13]. However, of all the approaches, fabrication of nanocomposite has been shown to enhance the gas sensing performance substantially [14]. In addition, nanostructures provide a high surface area for interaction with the gas molecules [15].

To improve the electrochemical performance and conductivity of the SnO<sub>2</sub> and NiO nanoparticles, the semiconducting materials are composed of NiSnO<sub>3</sub>/GNS and NiSnO<sub>3</sub> as electrodes. For instance, NiSnO<sub>3</sub> has been used in lithium-ion batteries as anode [16].

Previously, there has been some debate around the basic material properties of NiSnO<sub>3</sub>, like fundamental band gap [17]. Species with the general formula ABO<sub>3</sub>, where A is monovalent or divalent metal and B is a tetra- or pentavalent atom are mixed with perovskite to enhance their electrical characteristics [18-21].

Several methods have been used to produce NiSnO<sub>3</sub> thin films, such as hydrothermal process [22], green synthesis method [23], and chemical oxidation method. [24]. For large thin films, the spray pyrolysis (SP) method seems to be the most optimum technique owing to its low cost, simplicity and applicability with metal doping. This technique can be used to synthesize smooth, pinhole-free, and homogenous thin films [25].

In this study, we used the spray pyrolysis technique for the synthesis of perovskite-based thin films and nanocomposites with the aim to enhance the gas response. We used several analytical techniques to assess the performance of these films.

## 2. Experimental details

### 2.1 Preparation of NiO-SnO<sub>2</sub> nanocomposites and perovskite NiSnO<sub>3</sub> thin films

For the preparation of NiO-SnO<sub>2</sub> nanocomposites and perovskite NiSnO<sub>3</sub> thin films were nickel chloride hexahydrate (NiCl<sub>2</sub>.6H<sub>2</sub>O) and tin (II) chloride dehydrate (SnCl<sub>2</sub>.2H<sub>2</sub>O Merck extra pure). Nickel chloride hexahydrate and tin (II) chloride dehydrate were mixed at different ratios like 25:75, 50:50, and 75:25 (1:3, 1:1, and 3:1) (Table 1).

**Table 1:** Varying amount of reactants and spraying solutions

Sample No.	NiCl <sub>2</sub> .6H <sub>2</sub> O (cm <sup>3</sup> )	SnCl <sub>2</sub> .2H <sub>2</sub> O (cm <sup>3</sup> )	Volume Ratio	Reactants
S1	25	75	1:3	NiO-SnO <sub>2</sub>
S2	50	50	1:1	NiO-SnO <sub>2</sub>
S3	75	25	3:1	NiSnO <sub>3</sub>

Based on the composition, the prepared films were named as S1 and S2 (both NiO-SnO<sub>2</sub> nanocomposites), and S3 (perovskite-based NiSnO<sub>3</sub> thin films).

The formation of the film is critically dependent upon landing of the droplets, reaction, and evaporation of the solvent, all of which are dependent on the size of the droplets. We optimized the process parameters as listed in Table 2. The carrier gas pressure, to and fro nozzle movement and substrate temperature were kept constant during the process.

It is noteworthy that the ideal condition for film synthesis is the point where the droplet reaches close enough to the substrate for the solvent to evaporate entirely.

## 2.2 Optimized parameter

**Table 2:** Optimum parameter to obtain NiO-SnO<sub>2</sub> nanocomposites and pervoskite NiSnO<sub>3</sub> thin films.

Deposition parameter	Optimum value / item
Spray deposition time	10 min.
Nozzle-to-substrate distance	30 cm
Concentration of precursor	0.05 M
Solvent	Deionized water
Deposition temperature	400 °C
Flow rate of solution	8 mlmin <sup>-1</sup>
Annealing temperature	500 °C
Annealing time	1 hr

## 2.3 Film annealing

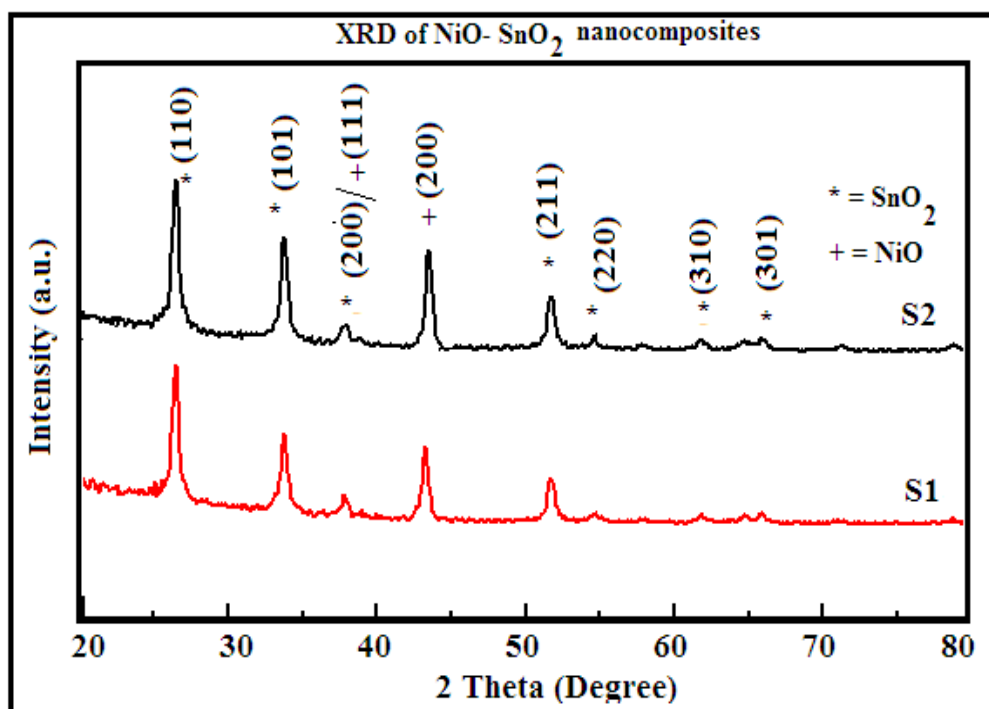
The NiO-SnO<sub>2</sub> nanocomposites and pervoskite NiSnO<sub>3</sub> thin films samples were annealed at 500 °C for 1 h in the presence of air to increase its micro-structural properties and gas sensing performance.

## 3. Materials characterization

### 3.1 Determination of film thickness

Measurement of thickness was conducted using surface profiler (AMBIOS Tech. (USA) XP.I). The thickness of the films were found to S1=789, S2 =890 and S3= 678 respectively. Thickness of the thin films were random it may be due to different volume proportion of the Ni and Sn (Different at% of Ni and Sn during the formation of the NiO-SnO<sub>2</sub> nanocomposites and pervoskite NiSnO<sub>3</sub> thin films).

### 3.2 XRD of NiO-SnO<sub>2</sub> nanocomposite thin films



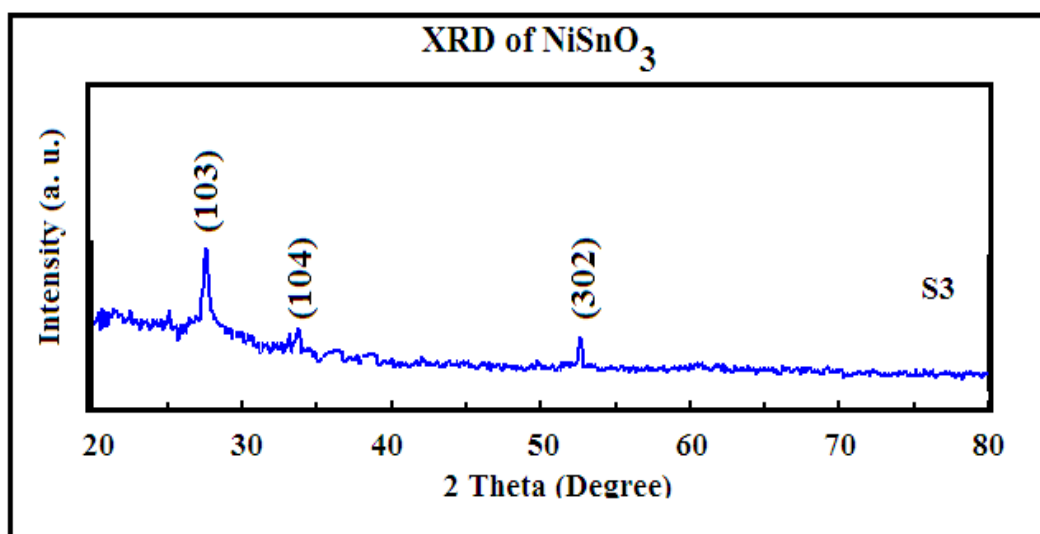
**Figure 1: X-ray diffractogram of nanocomposites thin films samples: S1 and S2**

The XRD was used to assess the structural properties of the thin films. The  $2\theta$  values were in the range of  $20^\circ$  to  $80^\circ$ . The XRD patterns of pure NiO indicate cubic structure (Chapter 3) and pure SnO<sub>2</sub> shows tetragonal structure (Chapter 4). The S1-S2 sample shows a mixture of phases of NiO (+) and SnO<sub>2</sub> (\*) (Fig. 1).

The XRD findings did not reveal presence of any impurities in the sample. The sharp diffraction peaks additionally indicated high sample purity. XRD pattern revealed the (from sample S1-S2) the formation of NiO-SnO<sub>2</sub> nanocomposites thin film. The NiO and SnO<sub>2</sub> diffraction peaks matched with standard value for NiO and SnO<sub>2</sub> [JCPDS data card no. 4-0835 (NiO) and JCPDS data Card no.21-1250 (SnO<sub>2</sub>)].

There is no shift of the diffraction line position for the nanocomposites thin film samples. The broad diffraction peaks indicates the nanocrystalline nature of the component crystal in nanoplates. Strong diffraction peaks confirm the presence of mixed phases of NiO and SnO<sub>2</sub> formations. The average crystallite size of NiO-SnO<sub>2</sub> nanocomposite-based thin film samples ranged between 12 nm and 14 nm as assessed using the Scherrer formula [20].

### 3.3 XRD of perovskite NiSnO<sub>3</sub> thin film



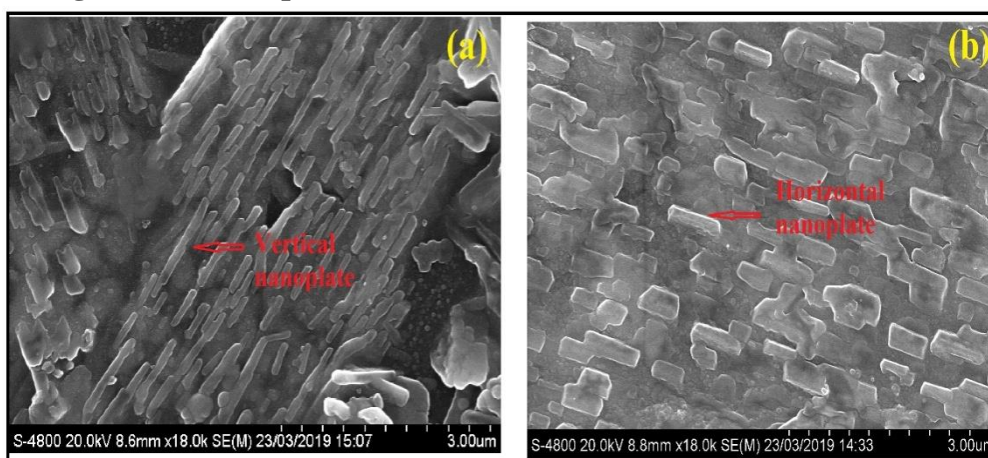
**Figure 2: X-ray diffractogram of perovskite NiSnO<sub>3</sub> thin film sample S3.**

The crystalline and phase structure of sample S3 was also examined using XRD (Fig. 2). The peaks (103), (104), and (302) corresponds to NiSnO<sub>3</sub> (JCPDS file no. 28-0711). No impurity phases were identified in the film sample. These XRD patterns confirm the formation and composition of perovskite NiSnO<sub>3</sub> thin film. Of all the peaks, the (103) peak is the predominant peak, which indicates preferential growth and that the surface of the substrate is perpendicular to the *c*-axis of the grains. This means that the grains have perpendicular to the substrate surface. It should be noted that low intensity of the peaks was observed indicating the formation of perovskite phase.

The average thickness of the films as calculated using the Debye-Scherrer formula [26] was 10 nm.

### 3.4 Surface morphology using FESEM

- FESEM images of nanocomposites NiO-SnO<sub>2</sub>



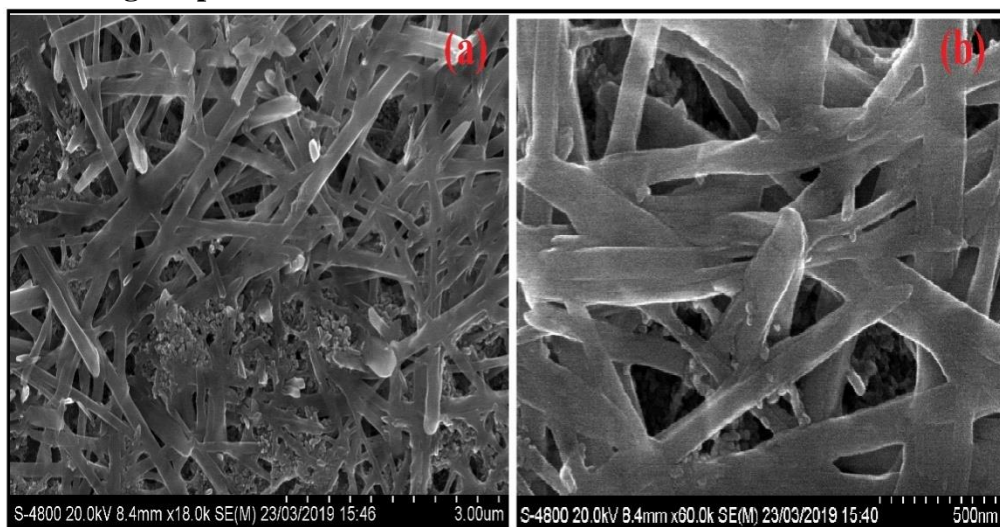
**Figure 3: FE-SEM images of NiO-SnO<sub>2</sub> nanocomposites thin films: S1 (a), S2 (b)**

We also examine the surface morphology of the films using FESEM. As shown in Fig. 3, irrespective of the volume ratios of Sn and Ni, the nanoplates were clearly defined across the whole substrate; however the vertical alignment of the nanoplate's orientation changed from horizontal alignment with respect to the volume ratio (1:3 and 1:1). The nanocomposite thin films (Fig. 3 (a)) exhibit vertically oriented nanoplates [27].

For volume ratio of 1:1, there was a slight distortion in the nanoplates, changing their alignment from vertical to horizontal (Fig. 3((b) (S2))).

The lengths of S1 and S2 nanoplates were 227 nm and 367 nm, respectively. The nanoplate structure will enhance the performance of these films.

### 3.5 FESEM image of perovskite NiSnO<sub>3</sub> thin film

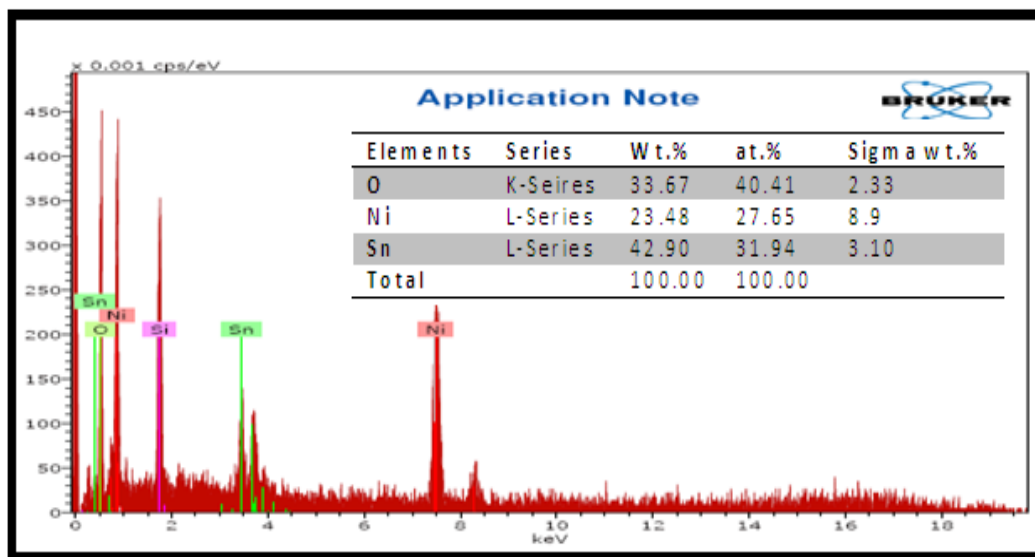


**Figure 4 (a) and (b): FESEM images of NiSnO<sub>3</sub> perovskite thin film: S3 (Different magnification power)**

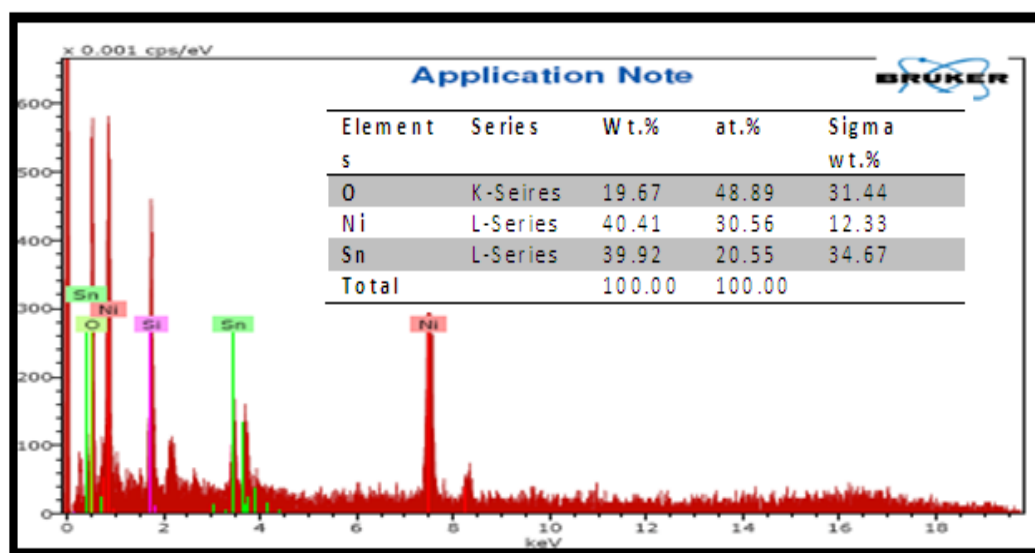
FESEM image of nanorod NiSnO<sub>3</sub> perovskite thin film (Sample=S3) is represented in Fig. 4. It appeared to be uniform distribution over the substrate and the corresponding low and high magnification image is shown in Fig. 4 (a) and (b). Nanorods are grown from vertically and horizontally aligned exhibits high-density nanorod. No other morphologies, such as nanopowders, nanoplates were formed. Fig. 4 (a) and (b) show the presence of several interconnected grains composed of nanorod with diameter 123-150 nm and lengths of 230-300 nm, indicating that these nanorod were produced on a large scale with uniform size and morphology. Fig 4 (b) at higher magnification, clearly reveals that the surface of the nanorod consists of many small nanoparticles.

### 3.6 Quantitative elemental analysis using EDAX

#### • EDAX spectra of NiO-SnO<sub>2</sub> nanocomposites



(a)



(b)

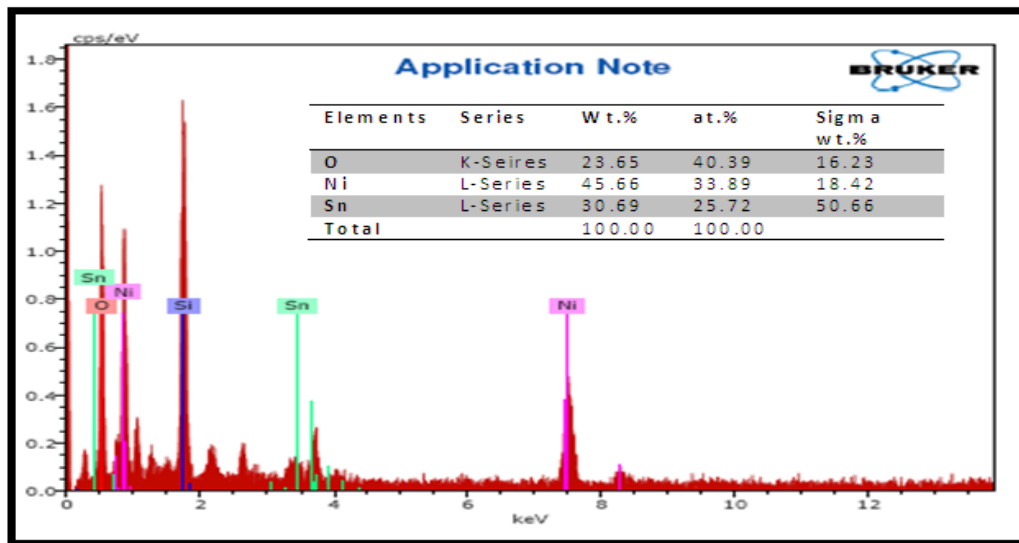
**Figure 5: EDAX spectra of NiO-SnO<sub>2</sub> nanocomposites thin film samples S1 (a) and S2 (b).**

We performed EDAX analysis to further elucidate the elemental composition of films (Fig. 5 (a) and (b)). Stoichiometrically expected at % of Ni, Sn and O for NiO-SnO<sub>2</sub> nanocomposite thin films are: 20.00, 20.00 and 60.00 respectively. Observed at % for NiO-SnO<sub>2</sub> nanocomposites thin films were inset in the EDAX spectra Fig 5 (a) and (b). Our findings showed that the conventional samples comprised Ni and O, while the comprised Ni, Sn, and O.

As volume ratio of Ni and Sn changes during the formation of nanocomposites thin films at % of Ni in Sn also changes. From the table inset in Fig. (5) shows that the prepared NiO-SnO<sub>2</sub> nanocomposites thin film were nonstoichiometric in nature.



- **EDAX spectra of NiSnO<sub>3</sub>**



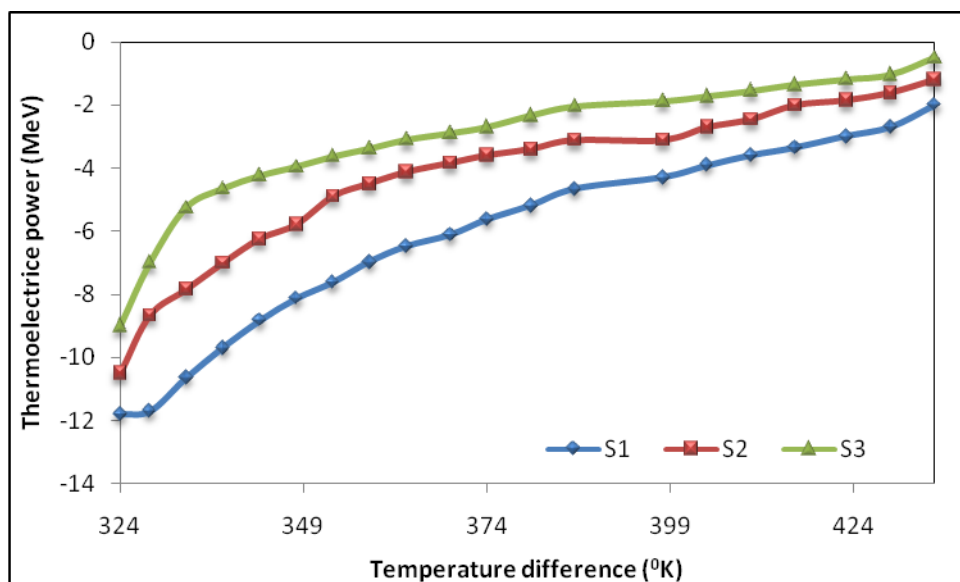
**Figure 6: EDAX spectra of NiSnO<sub>3</sub> perovskite.**

The constituent of elements in the thin film sample was conducted using EDAX spectra. Stoichiometrically expected at % of Ni, Sn and O for NiSnO<sub>3</sub> nanocomposites thin films is: 20.00, 20.00 and 60.00, respectively.

Observed at % for NiSnO<sub>3</sub> perovskite thin films were inset in the Fig 6 and it was observed to be nonstoichiometric in nature.

#### 4. Electrical properties

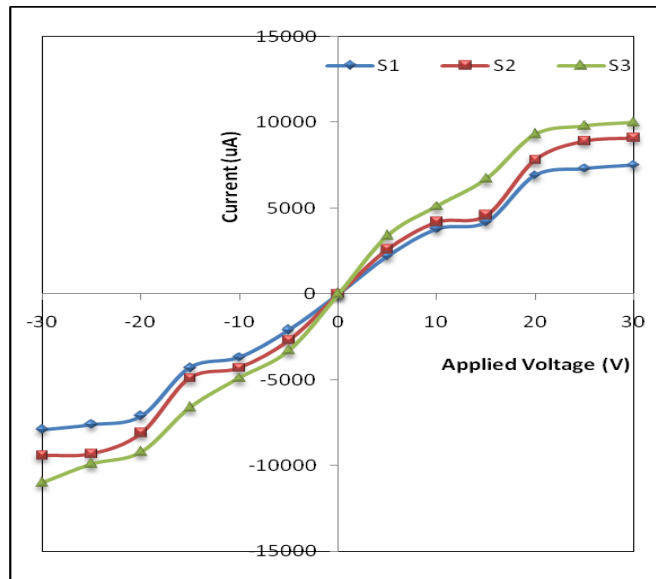
- **TEP measurement**



**Figure 7: TEP measurements of S1, S2, and S3**

From the TEP measurement (From Fig.7) it was found that as prepared nanocomposites and perovskite thin films was *n* type conductivity.

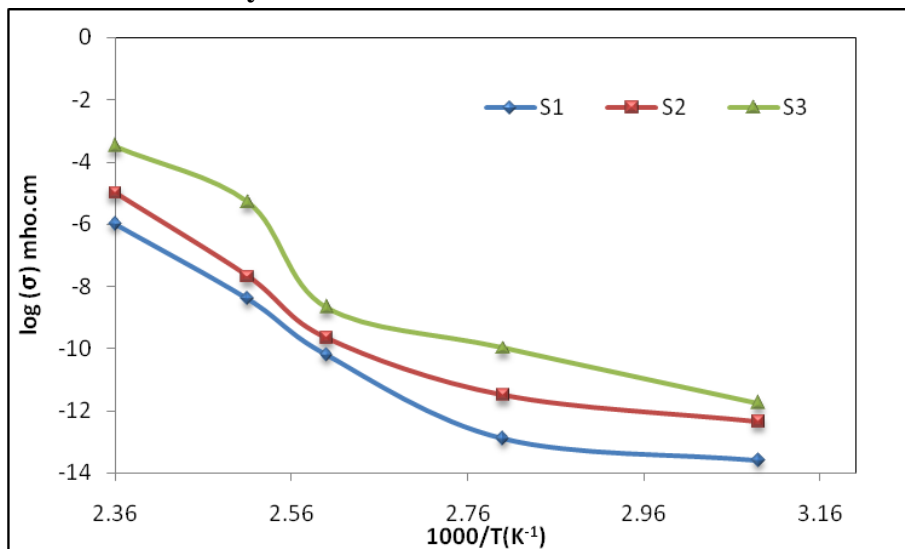
• **I–V characteristics**



**Figure 8: I–V characteristics of S1, S2, and S3**

The I-V characteristics of the samples were studied to examine the nature of contact (Fig. 8). The linearity observed in Fig. 8 shows that pressure contact has an ohmic nature [28].

• **Electrical conductivity**



**Figure 9: Log (σ) versus inverse of operating temperature (°K).**

For a given semiconductor, the thermal energy that is needed to transfer the electrons from the valence and to the conduction band is known as activation energy. We assessed the variation in conductivity ( $\sigma$ ) as a function of inverse of temperature (range: 323-423 K; Fig. 9). We observed a linear correlation between temperature and electrical conductivity ( $\sigma$ ). The Arrhenius law [29] was used to evaluate the activation energy of the film samples:

$$\sigma = \sigma_0 \exp (- \Delta E/kT) \text{----- (1)}$$



Where,  $\sigma$  = conductivity

$\sigma_0$  = conductivity constant

$k$  = Boltzmann constant

$T$  = Temperature

The thermal activation energies of S1, S2, and S3 were 0.10 meV, 0.28 meV, and 0.12 meV, respectively.

## 5. Conclusions

The spray pyrolysis method was used to build nanocomposites and perovskite thin films. XRD pattern indicates the formation of nanocomposites and perovskite thin films. Surface morphology studies confirm the formation of nanocrystalline nature of the prepared thin films. Elemental analysis revealed that the thin films were nonstoichiometric. Analysis of the microstructures revealed that the nanocomposites and perovskite thin films were nanostructure in nature. TEP profile indicates  $n$  type conductivity. I-V characteristics confirm ohmic contact of the thin films. Analysis of electrical conductivity revealed that the films were semiconducting. Furthermore, its other features, make them a promising material for the nanoscale gas sensors.

## Reference

- [1] Moreno-Fernandez G, Ibanez J, Rojo J M, Kunowsky M; Adv Mater Sci Eng Volume 2017, Article ID 3625414, [https://doi.org/10.1155/\(2017\)/3625414](https://doi.org/10.1155/(2017)/3625414).
- [2] Y .Zhu, X. Ji, Z .Wu, W. Song, H Hou, Z. X .Wu, Q .He, Chen, Banks CE;. J Power Sources (2014), 267:888.
- [3] P .Simon, Y .Gogotsi, Nat Mater; (2008), 7:845
- [4] JA Dirksen, K .Duval, TA Ring, Sens Actuators B, (2001), 80:106.
- [5] I .Hotovya, V. Rehaceka, P .Sicilianob, S .Caponec, L .Spiessd, Thin Solid Films; (2002), 418:9.
- [6] R. Sonker, A. Sharma, Md. Shahabuddin, M. Tomar, V. Gupta, Advanced Material Letter, 4, (2013), 196.
- [7] AK Singh, A. Janotti, M. Scheffler, CG .Van de Walle, Phys Rev Lett; (2008), 101:055502
- [8] A N Naje, A S Norry, A M Suhail, IJRSET, (2013), 2:7068.
- [9] S Das, V .Jayaraman, Prog Mater Sci; (2014), 66:112.
- [10] L N Moghadama, M Salavati-Niasari,. J Mol Struct; (2017), 1146:629.
- [11] H Mohd Faiz, M M Rahman, G Zaiping, C Zhixin, L Huakun, J Mater Chem; (2010), 20:9707.
- [12] P .Petronela, A .Anton, O .Niculae, P. Iulian, N .Valentin, S. Liviu, T Florin, Sens Actuators; (2016), 222:1024.
- [13] S. B. Patil, A. R. Bari, R. H. Bari, Material Focus, 3, (2014),119.
- [14] J. M. Patil, S. B. Patil, R. H. Bari, A. N. Sonar, International Letters of Chemistry, Physics and Astronomy, 53, (2015), 78.
- [15] Rajendra C. Pawara, Jin-Woong Leea, Vikas B. Patil b, Caroline S. Leea, Sensors and Actuators B, 187, (2013), 323– 330.

- [16] Mhamdi A, Dridi R, Arfaoui A, Awada C, Karyaoui M, Velasco-Davalos I A, Ruediger A, Amlouk M; *Opt. Mater*; **(2015)**, 47:386.
- [17] Yude W, Xiaodan S, Yanfeng L, Zhenlai Z, Xinghui W, *Solid State Electron*; **(2000)**, 44:2009.
- [18] Y. Li Liua, Y. Xingb, H. Feng Yanga, Z. Min Liua, Y. Yanga, G. Li Shena, R. Qin Yua, *Anal. Chim. Acta*, 527, **(2004)**, 21.
- [19] L. A. Patil, V. V. Deo, M. D. Shinde, A. R. Bari, M. P. Kaushik, *Sen. And actu. B: Chem.*, 160, **(2011)**, 243.
- [20] C. Xiangfeng, C. Zhiming, *Sens. And Actu. B Chem.*, 98, **(2004)**, 215.
- [21] R. H. Bari, S. B. Patil, *Sensors Letters*, 13, **(2015)**, 1.
- [22] P. E. Saranya, and S. Selladurai, *J Mater Sci.*; **(2018)**, 53:16022.
- [23] T. Athar, M. Abdelaal, Z. Khatoon, A. Kumar, A. Razzaq, A. Ahmad Khan, H. Fouad , S. Ahmed Ansari and Z. Amin Ansari, *Sensors and Materials*, Vol. 27, No. 7 **(2015)**, 563–573.
- [24] B. P Venkatesh, Kalyane Sangshetty, *International journal of electronics and communication engineering & technology (ijecet)*, Volume 5, Issue 11, November **(2014)**,06-.
- [25] J. M. Patil, S. B. Patil, R. H. Bari, and A. N. Sonar, *International Journal of Chem Tech Research*, Vol.8, No.3, **(2015)**, 1232.
- [26] D. S. Dalavi , N. S. Harale, I. S. Mulla, V. K. Rao, V. B. Patil, I. Y. Kim, J. H. Kim , P. S. Patil, *Materials Letters*;146, **(2015)**, 103.
- [27] S. S. Shendagea, V. L. Patilb, S. A. Vanalakarb, S. P. Patila, N. S. Haralea, J. L. Bhosaled, J. H. Kimc, P. S. Patil ,. *Sensors and Actuators B*, 240 **(2017)**, 426.
- [28] L. A. Patil, A. R. Bari, M. D. Shinde, V. Deo, *Sen. And actu. B, Chem.*79, **(2010)**, 149.