GLOBAL JOURNAL OF ENGINEERING SCIENCE AND RESEARCHES
CONDUCTOMETRIC AND ULTRASONIC STUDIES OF SUBSTITUTED ARYL BISTHIOUREA IN BINARY SOLUTION AT 300K TEMPERATURE

Ms. Smita V.Tambakhe[*1] & Dr.P.B.Raghuwanshi [2]
[*1]Assiatant Professor, Department of Science & Humanities, Sipna college of Engineering & Technology, Amravati, India
[2]Professor & Head, Department of Chemistry, Brijlal Biyani Science Collage, Amravati, India

ABSTRACT

Molar conductance of substituted aryl bisthiourea in binary solution such as Dioxane and water were studied by conductometric method. Its equivalent conductance and specific conductance values at various proportion of binary solution have been determined graphically. The Bisthiourea with solvent mixture were studied at various concentrations in combination of Dioxane-water mixtures such as 75%, 80%, 85% and 90% at different temperatures. Furthermore, these mixtures have been used to study acoustic parameters such as adiabatic compressibility, apparent molar volume, apparent molar compressibility, relative association, acoustic impedance, intermolecular free length. These parameters have been interpreted in terms of solute–solute and solute–solvent interactions and also structure making or breaking ability of solutes in the given binary solution.

Keywords: *Substituted aryl Bisthiourea, Binary solution, Conductometry, acoustic parameters.*

I. INTRODUCTION

Electrical conductivity has been measured in practice for more than 100 years and it is still an important and widely used analytical parameter today. The high reliability, sensitivity, fast response and the relatively low cost of the equipment make conductivity a valuable, easy to use tool for quality control. Electrical conductivity is a non-specific parameter over all dissolved ionic species (salt, acids, bases and some organic substances) in a solution. This means that this technique is unable to differentiate between diverse kinds of ions [1]. Conductometric studies provide useful and important indications of solvent structure, ion-solvent interaction and ion-ion interaction. Solvent composition plays a essential role in the conductivity of an electrolyte. In recent years there has been an increasing interest in the study of behaviour of electrolytes in partial and non aqueous solvents.

Solvent interactions may have predominant effects on solute-solvent interactions. The solute may get solvated preferentially by the any one of the solvent present in the binary solution. The solute- solvent interactions in water-organic media has been systematically reported by several researchers [2]. Considerable work has been reported on the solute-solvent interactions in water-organic media for measurements of acoustic parameters also. Ultrasonic velocities have been adequately employed in understanding the nature of molecular interaction in pure liquids [3], binary, and ternary mixtures [4-6]. The measurement of ultrasonic velocities finds extensive applications in understanding Physico-chemical behaviour of liquid mixtures. The molecular interactions in pure and binary liquid mixtures have been studied by measuring ultrasonic velocities by several researchers. The theoretical values of ultrasonic velocity have been evaluated by using Nomoto, impedance relation, Van Deal and Vangeel ideal mix relations, Junjie and Rao's Specific velocity relation and the results are interpreted in terms of molecular interactions.

In present study, conductometric and ultrasonic studies of substituted aryl Bisthiourea and Amidinothiocarbamide were carried out to study the solvent effects, the nature of ions and the ion-solvent interaction existing in the system, modification in the structure of a solvent due to the presence of an ion and ionic movement in a solution and also structure making or breaking ability of solutes in the given binary solution.

II. METHOD & MATERIAL

In the present study, the chemicals used were of A.R. grade. They were purified by recommended methods. All the weighing in the present study was made on Mechaniki Zakatasy Precyzynej Gdansk balance made in Poland. The densities of the solution were determined by standardize capillary pyknometer containing a bulb of volume of about 10 cm^3 and capillary having an internal diameter of 1 mm. An Ostwald's viscometer was used for the viscosity determination of pure liquid and liquid mixtures. The flow of time of pure liquid and liquid mixtures was measured using an accurate stop watch with a precision of ±0.1. The velocity of sound waves was found using an ultrasonic interferometer (Mittal Enterprises, New Delhi) at a fixed frequency of 1MHz with an accuracy of ±2ms^{-1}.

The equipment used for conductometric measurements is conductometer. For present work Conductivity meter no. EQ660A was used. A conductometer is an instrument for measuring complex resistances using alternating voltages in contrast to the measurement of the purely ohmic resistances of metallic conductors, liquids together with the measuring cell, constitute a network of resistances and capacities. The alternating voltages applied are available at minimum two frequencies by the appropriate selection of the measuring frequency, cell constant and electrode material. Under these conditions, the electrical conductivity can be determined from the measured resistance.

All the solutions for investigation were freshly prepared from the deionized water to avoid any ionic contamination. The 0.01M solution of each ligand was prepared in different percentage (75%, 80%, 85% and 90%) of 1,4-dioxane-water mixture. The density, viscosity and the ultrasonic velocity measurements of the ligand solutions were done at different temperature. In present study, results were discussed for 300K temperature.

For present investigation, following ligands were used L1: 1-phenyl bisthiourea
L2: p-tolyl bisthiourea
L3: p-chlorophenyl bisthiourea

III. RESULT & DISCUSSION

These experimental values are used to measure various acoustic parameters such as adiabatic compressibility (βs), Apparent Molar compressibility (φk), Specific acoustic impedance (Z), Intermolecular free length (Lf), Relative association (RA). These measurements are presented in Tables 1, 2 & 3. The variation of ultrasonic velocity (u) densities (ρ) and conductivities with volume component percentage of the systems of 1,4 dioxane are shown in graph.

The following formulae were used to calculate the conductometric and acoustical parameters.

Conductometric Parameter

Conductivity: Electricity is the flow of electrons. This indicates that ions in solution will conduct electricity. Conductivity is the ability of a solution to pass current. The conductivity reading of a sample will change with temperature.

$\kappa = G \times K$

Where, κ = conductivity (S/cm)

G = conductance (S), where G = 1/R
K = cell constant (cm^{-1})

Molar conductivity (Λm): The molar conductivity is defined as the conductivity produced by dissolving 1 gram-mole of an electrolyte placed between two large electrodes at one centimetre apart.
$\Lambda m = \kappa \frac{1000}{}$

31

C

Where,

Λm = Molar conductivity (Sm^{-1})

κ = Observed Conductance (S)

C = molarities of solution in g mole per litre.

Equivalent conductivity (Λeq): The equivalent conductivity is defined as the conductivity produced by dissolving 1 gram equivalent of an electrolyte placed between two large electrodes at one centimetre apart.

$\Lambda eq = \kappa \dfrac{1000}{C}$

Where, Λeq = Equivalent conductivity (equiv.ohm^{-1})

κ = Observed Conductance (S)

C = normalities of solution (equiv per litre))

Ultrasonic Parameter
Ultrasonic velocity and related parameters are adiabatic compressibility (β), apparent molar compressibility (ϕk), Intermolecular free length (Lf), Relative association (RA), Specific acoustic impedance (Z) and apparent molar volume (ϕv).

Adiabatic compressibility (β): A number of theoretical equations relating the ultrasonic velocity and other molecular properties have been established. Velocity of propagation of mechanical disturbances has to be considered a basic property of liquids in a molecular kinetic theory. By measuring ultrasonic velocity (U) and density (d) experimentally, the adiabatic compressibility (β) can be evaluated by using Laplace's equation.

$\beta = \dfrac{1}{U^2 d}$

Apparent molar compressibility (ϕk): It is an acoustic property which determined by measuring density and ultrasonic velocity that depends on the molarities of solution and molecular weight of the solute by the relation,

$\phi k = 1000 \times \dfrac{\beta s d o - \beta o d s}{m \times d s \times d o} + \dfrac{\beta s \times M}{d s}$

Where, do = density of pure solvent

ds = density of solution

m = molarity of solution

M = molecular weight of solute

βo = adiabatic compressibility of pure solvent and

βs = adiabatic compressibility of solution.

Intermolecular free length (Lf): It is one of the important acoustic properties to study the intermolecular interactions. Intermolecular free length has been evaluated from adiabatic compressibility (β) by Jacobson's formula,

$$\mathbf{Lf} = K\sqrt{\beta}$$

Where, K is the temperature dependent constant known as Jacobson's constant and is independent of the nature of liquid. Examining very large number of liquids, Jacobson obtained values of K at various temperatures. In obtaining these values for 'K' Jacobson has taken sound

velocity (U) in m/s, the density in g/cc and free length (Lf) in A^0.

Relative association (RA): It is a function of ultrasonic velocity and is computed by the equation,

$$RA = \frac{ds}{do} \times \left(\frac{Uo}{Us}\right)^{1/3}$$

Where, Uo and Us are ultrasonic velocities in solvent and solution.

Specific acoustic impedance (Z): It is determined from the measurement of ultrasonic velocity and density by formula,

$$Z = Us \times ds$$

The solute-solvent interactions may be interpreted in terms of acoustic impedance.

Apparent molar volume (φv): Along with the above acoustic properties , the apparent molar volume was also determined which does not depend upon ultrasonic velocity but depends upon densities of solution and solvent, molecular weight of solute (M) and molarity of solution (m). It is given by the relation,

$$\Phi_v = \frac{M}{ds} \times \frac{(do - ds) \times 10^3}{m \times ds \times do}$$

Where, M is molecular weight of solute and

m is molarity of solution

do and ds are densities of pure solvent and solution respectively.

Table 1: Ligand L1: 1-phenyl Bisthiourea

Temp. = 300K   Conc.= 0.01M   Ultrasonic Frequency: 1MHz

% Dioxane	Λm (S)	Λeq(cm²eq⁻¹ohm⁻¹)	ds x 10³ (Kg.m⁻³)	U (m/sec)	βs x 10⁻¹⁰ (pa⁻¹)
75	0.21	0.258	0.9882	1453.592	4.7892
80	0.12	0.147	0.9823	1444.000	4.8822
85	0.09	0.110	0.9823	1438.408	4.9203
90	0.02	0.024	0.9882	1422.408	5.0015
% Dioxane	**Φk x 10⁻⁶ (m³mol⁻¹pa⁻¹)**	**Φv x 10⁻⁵ (m³mol⁻¹)**	**RA**	**Lf x 10⁻¹¹ (m⁻¹)**	**Z x 10³ (kg m⁻²sec⁻¹)**

75	-9.7891	1.0092	1.0042	4.5164	1436.439
80	-8.5148	1.0158	1.0004	4.5600	1418.441
85	-8.1344	1.0158	1.0017	4.5777	1412.948
90	-7.6661	1.0092	1.0115	4.6154	1405.623

Table 2: Ligand   L2: p-tolyl Bisthiourea

Temp. = 300K   Conc.= 0.01M   Ultrasonic Frequency: 1MHz

% Dioxane	Λ_m (S)	Λ_{eq}(cm^{2}eq^{-1}ohm^{-1})	ds x 10^3 (Kg.m^{-3})	U (m/sec)	β_s x 10^{-10} (pa^{-1})
75	0.28	0.344	0.9776	1511.976	4.4745
80	0.17	0.209	0.9764	1451.200	4.8631
85	0.14	0.172	0.9752	1430.376	5.0119
90	0.07	0.086	0.9711	1495.224	4.6060
% Dioxane	**Φ_k x 10^{-6} (m^{3}mol^{-1}pa^{-1})**	**Φ_v x 10^{-5} (m^{3}mol^{-1})**	**RA**	**Lf x 10^{-11} (m^{-1})**	**Z x 10^3 (kg m^{-2}sec^{-1})**
75	-12.3177	1.0212	0.9805	4.3654	1478.107
80	-8.3616	1.0226	0.9928	4.5511	1416.951
85	-6.8036	1.0240	0.9964	4.6201	1394.902
90	-10.6238	1.0288	0.9776	4.4291	1452.012

Table 3: Ligand L3: p-chlorophenyl Bisthiourea

Temp. = 300K   Conc.= 0.01M   Ultrasonic Frequency: 1MHz

% Dioxane	Λ_m (S)	Λ_{eq}(cm^{2}eq^{-1}ohm^{-1})	ds x 10^3 (Kg.m^{-3})	U (m/sec)	β_s x 10^{-10} (pa^{-1})
75	0.32	0.393	0.9782	1504.008	4.5193
80	0.21	0.258	0.9735	1502.424	4.5507

% Dioxane	$\Phi k \times 10^{-6}$ $(m^3 mol^{-1}pa^{-1})$	$\Phi v \times 10^{-5}$ $(m^3 mol^{-1})$	RA	$Lf \times 10^{-11}$ (m^{-1})	$Z \times 10^3$ $(kg\ m^{-2}sec^{-1})$
85	0.16	0.196	0.9729	1492.856	4.6120
90	0.32	0.024	0.9723	1455.184	4.8569
75	-11.9051	1.0205	0.9828	4.3872	1471.220
80	-11.3167	1.0260	0.9785	4.4024	1462.609
85	-10.6681	1.0267	0.9799	4.4320	1452.399
90	-8.1842	1.0274	0.9877	4.5481	1414.875
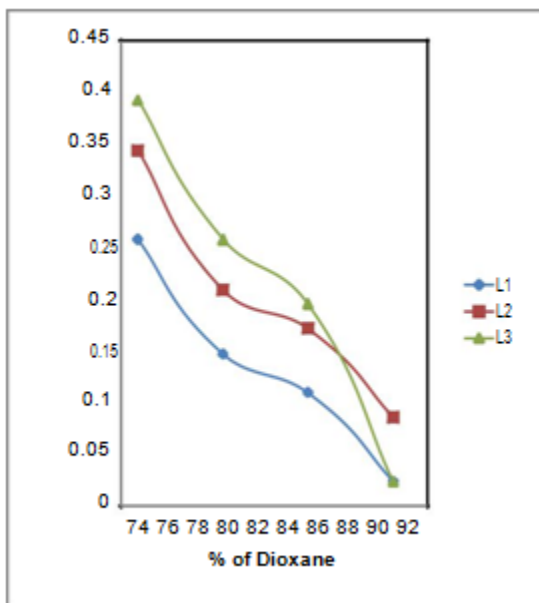
Figure 1: % of Dioxane Vs Equivalent conductance
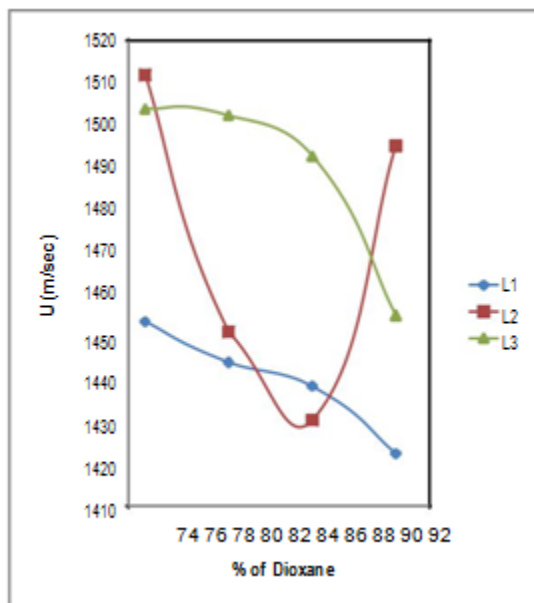
Figure 2: % of Dioxane Vs Ultrasonic velocity
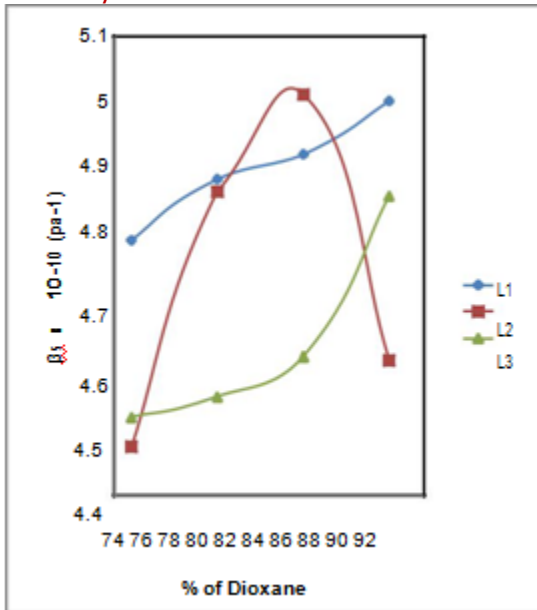
Figure 3: % of Dioxane Vs Adiabatic compressibility
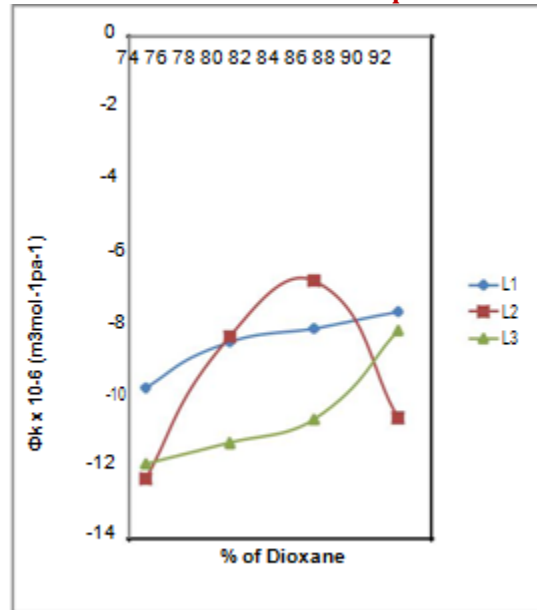
Figure 4: % of Dioxane Vs Adiabatic molar compressibility
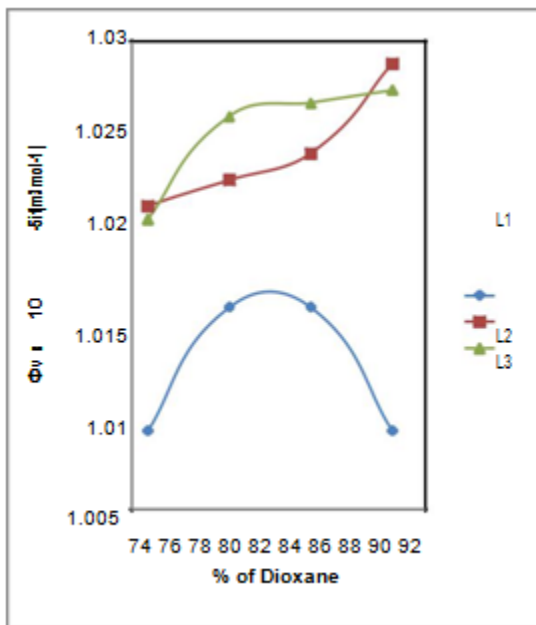
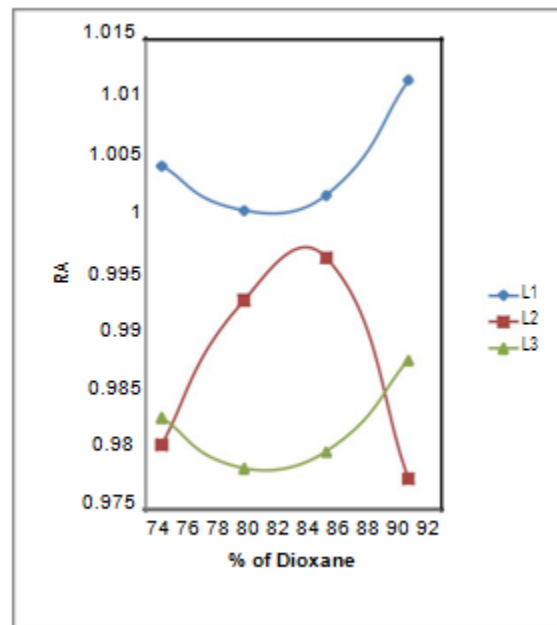*Figure 5: % of Dioxane Vs Adiabatic molar volume*

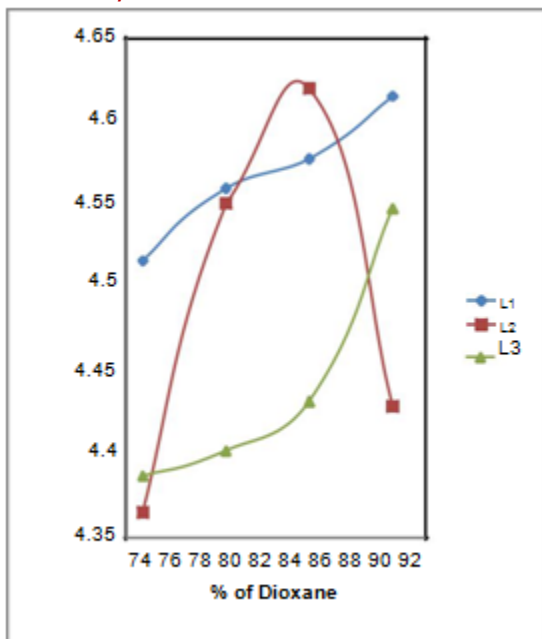*Figure 6: % of Dioxane Vs Relative association*

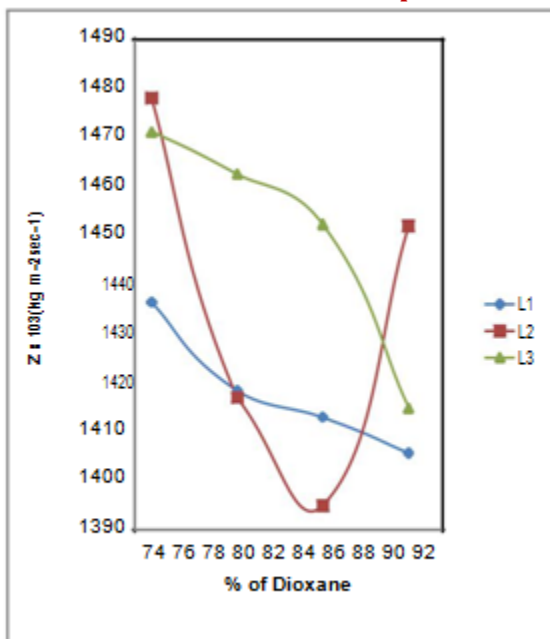*Figure 7: % of Dioxane Vs Intermolecular Free length*

Figure 8: % Dioxane Vs Acoustic Impedance

From figure 1, it was observed that the equivalent conductance of an electrolyte increases with decrease in concentration or increase in dilution. The equivalent conductance of strong electrolytes as well as weak electrolytes increases as well as decreases with concentration or increase in dilution. Concentration of electrolyte is inversely proportional to conductance. It is observed that all the ligands show increasing value of conductance with increase in the dilution at 300K.

From figure 2, it was found that the ultrasonic velocity (U) decreased with the increase in concentration of 1,4 Dioxane and water mixture. It happened because there was significant interaction between ions and solvent molecules suggesting a structure promoting behaviour of the added solvent mixture. Variation of ultrasonic velocity in solution depends upon the increase or decrease of molecular free length after mixing the component.

The adiabatic compressibility (βs) increased with the increase in concentration of solution. It happened due to collection of solvent molecule around ions, this supporting weak ion-solvent interaction. This indicates that there is significant solute- solvent interaction (figure 3). It was found that the value of apparent (molar) adiabatic compressibility (Φk) was increased with increase in concentration of ligands in dioxane. It shows strong electrostatic attractive force in the vicinity of ions(figure 4). It was observed that apparent molar volume (Φv) increased with concentration in both systems. It indicates the existance of strong ion-solvent interaction (figure 5). Relative association (RA) is influenced by two factors (i) the breaking up of the solvent molecules on addition of electrolyte to it resulting in decrease in value of RA and (ii) the solvation of ions that are simultaneously present, resulting in increase in the value of RA . It was observed that the value of relative association (RA) increased with the increased in concentration. It has found that there was strong interaction between solute and solvent. The increase of RA with concentration suggests that solvation of ions predomonates over the breaking up of the solvent aggegates (1,4 Dioxane-water) on addition of substituted Bisthioureas(figure 6).

Intermolecular free length (Lf) is an important parameter that has association with adiabatic compressibility (βs). It is clear that the intermolecular free length shows a similar behavior as reflected by 'βs'. Moreover, free length is a predominant factor in determining the variation of ultrasonic velocity in solutions. The inter dependence of 'Lf' and 'U' has been evolved from a model for sound propagation proposed by Eyring and Kincaid. According to the proposed theory, the increase in the value of 'βs' and 'Lf' with decrease in ultrasonic velocity further strengthens the

37

process of complex formation between the solute molecules due to which structural arrangement is considerably altered. In the present study also, there is a possibility of complex formation due to interactions as revealed by the nonlinear variation of ultrasonic velocity and their related parameters due to strong interaction of forces (figure 7).

The acoustic impedance is the parameter related to the elastic properties of the medium. Therefore, it is important to examine specific acoustic impedance in relation to concentration and temperature. From data, it shows the variation of acoustic impedance with concentration. In the present study, the specific acoustic impedance (Z) decreased with the increase in concentration in dioxane and water mixture. When concentration of electrolyte was increased, the thickness of oppositely charged ionic atmosphere increases due to decrease in ionic strength. This is suggested by decrease in acoustic impedance with increase concentration (figure 8).

IV.   CONCLUSION

The present study shows the experimental data for conductance, ultrasonic velocity and density at 300K for substituted Bisthiourea in 1,4 dioxane and water binary solution. Concentration of electrolyte is inversely proportional to conductance therefore It is observed that all the ligands show increasing value of conductance with increase in the dilution at 300K. From experimental data, the acoustical parameters were calculated and the solute-solvent interaction and ion-ion / solute-solute interaction existing between solute and 1,4dioxane were also studied. Lastly it has been concluded that the solute-solvent interaction in aryl substituted bisthiourea and binary solution systems are weak.

V.   ACKNOWLEDGEMENT

REFERENCES
1. *T.Moeller,D.F.Martin,W.S.Randall,L.C.Tomson,Chem.Rew.1,1965,pp.57.*
2. *.Jagan Raj, J.Subha, S.Bangaru, S.Alwar and P.S Raghavan,"The electrical Conductivity of HCl in Binary Solvent mixtures-A Probe for its Molecular Interaction studt" International Journal of Advances ChemicalScience and Applications,2(1),2014,pp.34-40*
3. *K.V.Lakshmi, D.Suhasini, M.J.Reddy, C.Rani, K.C.Rao, M.C.Subha,"Ultrasonic studies on binary liquid mixtures of tetrahydrofuran with benzenes at 308.15K", Indian Journal of Advances in Chemical Science,3,2014,pp.38-48.*
4. *P.Nagaraja, C.N.Rao, P.Venkateswarlu,"Excess volumes of binary liquid mixtures of m-xylene with nitrotoluenes",Indian Journalof Advances in ChemicalScience,4,2016,pp.421-424.*
5. *J.N.Spencer, E.Jeffrey, C.Robert,"Enthalpies of solution and transfer enthalpies an analysis of the pure base colorimetric method for the determination of hydrogen bond enthalpies",The Journal of PhysicalChemistry,1979,83,pp.1249.*
6. *R.J.Rort,W.R.Moore,"Viscosities of binary liquid mixtures",Transactions of the Faraday Society,62,1966,pp.1112.*