



# ULTRASONIC INTERFEROMETRIC INVESTIGATIONS OF 1-(2-HYDROXY-3-SUBSTITUTED-5-CHLOROPHENYL) ETHENYL DIPHENYL ENAMINES IN DIOXANE MEDIUM

P. B. RAGHUVANSHI\* and A. D. DESHMUKH

Department of Chemistry, Brijlal Biyani Mahavidyalaya, AMRAVATI – 444604 (M.S.) INDIA

## ABSTRACT

Ultrasonic velocity and density measurements of ligand, 1-(2-hydroxy-5-chlorophenyl) ethenyl-diphenyl enamines ( $L_1$ ), 1-(2-Hydroxy-3-nitro-5-chlorophenyl) ethenyl diphenyl enamines ( $L_2$ ) were carried out in dioxane solvents. To investigate solute-solvent, solute-solute interaction solute solvent, solute-solute interaction at 303 K. Adiabatic compressibility ( $\beta$ ), Apparent molar compressibility ( $\phi_k$ ), Apparent molar volume ( $v$ ), Intermolecular free length ( $L_f$ ), Relative association ( $R_A$ ) were determined. The acoustic parameters were obtained for ligands  $L_1$ ,  $L_2$  in dioxane solvent at different concentrations. The effect of different substituents in this solvent i.e. dioxane and the effect of dilution on ligand solution were investigated.

**Key words:** Enamines, Solute-solvent interactions, Interferometric investigation.

## INTRODUCTION

Ultrasonic measurements have been widely applied to explore information regarding internal structure, molecular association, complex formation, internal pressure and stability of coordination complexes<sup>1</sup>. Ultrasonic velocity and density measurements of 2-hydroxy- $\alpha$ -bromoacetophenones and 2-(4'-H/chloro)-benzylidene-5-methyl-7-substituted coumarone-3-ones were carried out in ethanol and dioxane respectively for solute-solvent, solute-solute interactions. These interactions were also performed with Cd (II) and Fe (III) metal ions at 303.15 K. The data obtained during the study is used for determining the most significant acoustic parameters like apparent molar compressibility ( $\phi_k$ ) and specific acoustic impedance ( $z$ ). These parameters explore solute-solute and solute-solvent interactions in different solvent<sup>2</sup>. Ultrasonic parameters are being extensively used to study molecular interaction in pure liquids<sup>3-5</sup>, liquid mixture<sup>6-8</sup> and electrolyte solution<sup>9</sup>. Ultrasonic velocity

---

\* Author for correspondence; E-mail: desh mukhashwini16@gmail.com

in 1,3-dioxane-water mixture has been measured by Baumgartner and Atkinson<sup>10</sup>. Ultrasonic velocity of water-dioxane solutions of tetracycline hydrochloride and chlorotetracycline at 298.15 K and 308.15 K were measured by Pandey et al.<sup>11</sup> Ultrasonic velocity and densities of 3-(2-hydroxy-3-bromo-5-methylphenyl)-5-phenyl isoxazole ( $L_1$ ), 1-phenyl-3-(2-hydroxy-3-bromo-5-methyl phenyl)-5-(4-methoxy phenyl) pyrazoline ( $L_2$ ) in dioxane and different percentage of dioxane-water mixtures at different temperatures (303, 308, 313, 323 K) have been evaluated at 0.01 M concentration<sup>12</sup>.

The molecular interaction between solute-solute and solute solvent was studied the help of acoustic properties determined by ultrasonic interferometer at 303.15 K in polar acetone and non polar dioxane solvents<sup>13</sup>. The effect of introduction of metal ions viz Cu (II), Fe (III) in the same solution was found out. Also the effect of position of same group at ortho and para position on the molecular interaction was simultaneously examined.

Description of hydroboration of enamines in chronological order covering early work to give  $\beta$ -amino alcohols and reduction products and then our more recent work to give  $\beta$ -aminoorganobromones and their subsequent conversion into  $\beta$ -amino alcohols,  $\beta$ -aminoboronic esters and acids, and olefins<sup>14</sup>. Analytical method to determine the enantiomeric excess (ee) of the  $\beta$ -amino alcohols obtained from the asymmetric hydroboration of enamines are also described.

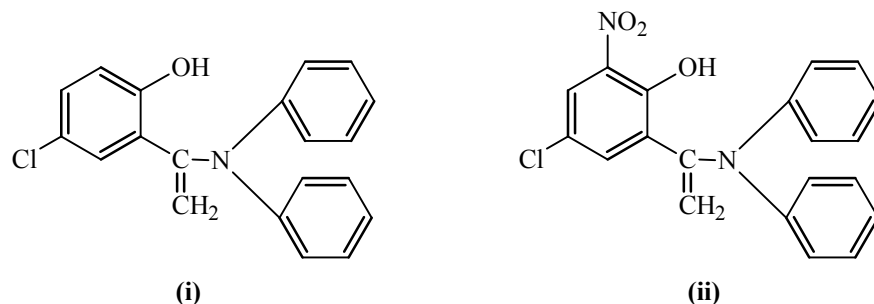
We intended to analyze study of these ligands in dioxane solvents to investigate protic-aprotic nature, polarity-non-polarity, hydrogen bonding, dielectric constant and density of solvent on solute-solvent, ion-solvent and ion-ion interaction. Hence, in this present investigation attempt is made to understand behaviour of substituted enamines viz. 1-(2-hydroxy-5-chlorophenyl) ethenyl-diphenyl enamines ( $L_1$ ), 1-(2-hydroxy-3-nitro-5-chlorophenyl) ethenyl diphenyl enamines ( $L_2$ ) compounds in dioxane solvent with respect to  $v$ ,  $d$ ,  $\beta_s$ ,  $\phi_k$ ,  $\phi_v$ ,  $L_f$ ,  $R_A$ .

## EXPERIMENTAL

All the chemicals were of A. R. grade.

- (i) 1-(2-hydroxy-5-chlorophenyl) ethenyl-diphenyl enamines ( $L_1$ )
- (ii) 1-(2-hydroxy-3-nitro-5-chlorophenyl) ethenyl diphenyl enamines ( $L_2$ )

These enamines are synthesized by known method<sup>15</sup>.



The solvent 1,4-dioxane were purified by standard procedure<sup>16</sup>. Densities were measured with the help of bicapillary pycnometer, 0.001 M solution of ligand in dioxane solvent. Weighing was made on Mechaniki Zaktady Precynyneij Gdansk balance made in Poland ( $\pm 0.001$  g). A special thermostatic arrangement was done for density and ultrasonic velocity measurements. Elite thermostatic water bath was used, in which continuous stirring of water was carried out with the help of electric stirrer and temperature variation was maintained within  $\pm 0.1^\circ\text{C}$ . Single crystal interferometer (Mittal Enterprises, Model MX-3) with accuracy 1 MHz was used in the present work. The densities and ultrasonic velocity of ligands in dioxane solvent at 303 K.

## RESULTS AND DISCUSSION

In the present investigation, measurements of densities and ultrasonic velocities of  $L_1$  and  $L_2$  in dioxane had been carried out and given in Table 1.

**Table 1: Acoustic parameters for ligands in dioxane at 303 k. [Freq. = 1 MHz]**

	$v$ (m sec. <sup>-1</sup> )	$d$ (Kg m <sup>-2</sup> )	$\beta \times 10^{-4}$ (pa <sup>-1</sup> )	$\phi_v$ (m <sup>3</sup> mol <sup>-1</sup> )	$\phi_k$ (m <sup>3</sup> mol <sup>-1</sup> pa <sup>-1</sup> )	$L_f \times 10^{-2}$ (Å)	$R_A$
Dioxane	385.07	1171	78.973				
$L_1$ -Dioxane (0.005 M)	407.47	1162.5	70.017	1.249094	-0.144219	50.37	0.974206
$L_2$ -Dioxane (0.005 M)	401.24	1158.7	71.972	1.813355	-0.106521	51.07	0.976021
$L_1$ -Dioxane (0.0025 M)	480.8	1158	50.093	3.835035	-0.967279	42.6	0.918354
$L_2$ -Dioxane (0.0025 M)	400.71	1161.3	72.324	2.853503	-0.206468	51.19	0.978642

Cont...

	$\nu$ (m sec. <sup>-1</sup> )	$d$ (Kg m <sup>-2</sup> )	$\beta \times 10^{-4}$ (pa <sup>-1</sup> )	$\phi_v$ (m <sup>3</sup> mol <sup>-1</sup> )	$\phi_k$ (m <sup>3</sup> mol <sup>-1</sup> pa <sup>-1</sup> )	$L_f \times 10^{-2}$ (Å)	$R_A$
L <sub>1</sub> -Dioxane (0.00125 M)	448.93	1161	57.607	5.884659	-1.425765	45.69	0.942025
L <sub>2</sub> -Dioxane (0.00125 M)	418.44	1164.7	66.519	3.695698	-0.82621	49.09	0.967444

### Adiabatic compressibility ( $\beta$ )

Adiabatic compressibility is one of the important properties during the study of solute-solvent interactions and represented by  $\beta$ .

It was observed from tables that the values of adiabatic compressibilities of ligand L<sub>1</sub> and L<sub>2</sub> increases as the concentration increases. At 0.05 x 10<sup>-2</sup> M concentration both L<sub>1</sub> and L<sub>2</sub> ligand shows higher value of adiabatic compressibility. L<sub>2</sub> ligand solution shows higher value of adiabatic compressibility than L<sub>1</sub> ligand.

$$L_1 - \text{dioxane} < L_2 - \text{dioxane}$$

In L<sub>1</sub> ligand solution at 0.125 x 10<sup>-2</sup> M concentration  $\beta$  value increases and again decreases. This irregular trend of value is due to the effect of different substituents attached to heterocyclic ring and due to effect dilution.

L<sub>1</sub> and L<sub>2</sub> ligands have different structures L<sub>2</sub> ligand have more substituents attached to different position than the L<sub>1</sub> ligand which have lesser substituent.

It was seen from the table that the  $\beta$  value of L<sub>2</sub> are higher than L<sub>1</sub>, this may be due to change in structure of ligand.

L<sub>2</sub> is such a ligand having only strong electron withdrawing group (-NO<sub>2</sub>) near to (-OH) group, (-Cl) is attached to fifth position of both the L<sub>1</sub> and L<sub>2</sub> ligands. This cause strong (-I) effect<sup>17</sup>.

In both the ligands i.e. L<sub>1</sub> and L<sub>2</sub> electron releasing group (-C=CH<sub>2</sub>) is also present.

The present investigation reveals that the nature of ring structure, total number of different atoms present in the ring, resonance stabilization in the ring and electron donating and electron withdrawing substituent present nearer to -OH group on the ligand will directly

interfere the interaction between solute and solvent and show change in adiabatic compressibility.

### **Apparent molar compressibility ( $\phi_k$ )**

Apparent molar compressibility ( $\phi_k$ ) is another important acoustic parameter, which explains the solute-solvent and solute-solute interactions in solutions.

$$\phi_k = [1000 (\beta_s d_o - \beta_0 ds)/m ds d_o] + (\beta_s M/ds)$$

Thus, the structure of solute and the number of atoms present in it will have direct effect on  $\phi_k$  values. It is observed that  $\phi_k$  values are negative for all composition of dioxane. This interpret in terms of loss of compressibility of solute due to strong electrostatic solvation of ions.

Kaulgud et al.<sup>18</sup> have discussed interaction of polar -OH group in carbohydrate solution in terms of  $\phi_k^0$  and  $\phi_v^0$  values. Negative values of  $\phi_k$  shows that interactions are insensitive to solvent. It could be also explained by postulating the polar -OH group interact with the surrounding organic solvent through dipole-dipole interaction in such a way that the surrounding solvent molecule loses its own compressibility to a certain extent.

### **Apparent molar volume ( $\phi_v$ )**

Apparent molar volume is the thermodynamic property of solutions, which express the solute-solvent interactions, and it is obtained from the density and molality of solution and the molecular weight of the solute.

It was observed from the table that the  $\phi_v$  values of L<sub>1</sub> ligand solution is higher than L<sub>2</sub> ligand at different concentrations.

$$L_1 - \text{dioxane} > L_2 - \text{dioxane}$$

The  $\phi_v$  values for ligand L<sub>1</sub> and L<sub>2</sub> at 0.5 x 10<sup>-2</sup> M concentration is lower and when the concentration decreases the  $\phi_v$  value for L<sub>1</sub> and L<sub>2</sub> ligand increases i.e. at more dilution of dioxane ligand shows higher values.

Higher  $\phi_v$  value may be due to the presence of electron donating nature of ligand.

Weak solute-solvent interaction is there as oxygen in dioxane also possesses negative charge. It results in an increase in  $\phi_v$ , as the percentage of dioxane in ligand solution increases.

### **Intermolecular free length ( $L_f$ )**

$L_f$  is one of the important acoustic properties to study the intermolecular interactions. From the table it can be noted that ligand  $L_2$  have higher value than  $L_1$  at different concentration in dioxane medium.

$$L_1 - \text{dioxane} > L_2 - \text{dioxane}$$

At higher concentration ligand  $L_1$  and  $L_2$  shows higher value and as the concentration decreases values are decreases. Ligand  $L_1$  at  $0.25 \times 10^{-2}$  M concentration shows less value than ligand  $L_1$  at  $0.125 \times 10^{-2}$  M concentration. This may be due to non-polar nature the compact packing of molecules is already there and when polar solute is added because of its association again free space decreases. Therefore, the  $L_f$  values in dioxane must be smaller.

### **Relative association ( $R_A$ )**

$R_A$  is an acoustic property of understanding interaction, which is influenced<sup>19</sup> by two opposing factors.

- (i) Breaking of solvent structure on addition of solute to it, and
- (ii) Solvation of the solutes that are simultaneously present by the free solvent molecules.

From the table it is clearly seen that the  $R_A$  value decreases and then increases. At higher concentration of solute, the breaking up of solvent occurs resulting in decrease of  $R_A$  value, which is interpreted by first factor whereas the increases in  $R_A$  on increasing % of solvent i.e. dioxane at more dilution. This explained by second factor. In the present investigation, the value of  $R_A$  for ligand  $L_2$  is more than ligand  $L_1$  at different concentration in dioxane.

By using ultrasonic interferometric study,  $\beta$ ,  $\phi_k$ ,  $L_f$ ,  $\phi_v$ ,  $R_A$  etc. acoustic properties are determined, which explain how these interactions occur and responsible for breaking and making of the structure in the solution, so in the present work these acoustic parameters were studied for already synthesized ligands, which are used as solutes.

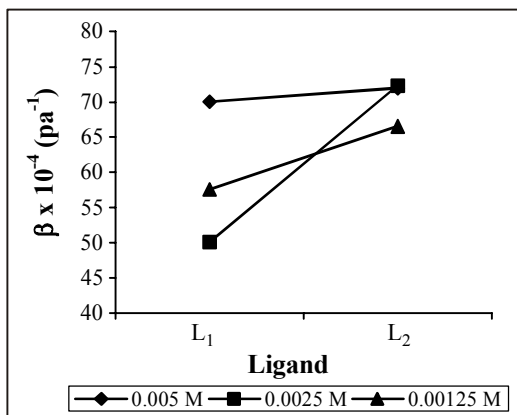


Fig. 1: Adiabatic compressibility of  $L_1$  and  $L_2$

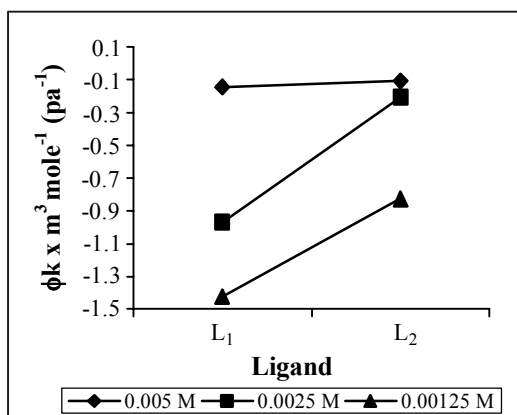


Fig. 2: Apparent molar compressibility of  $L_1$  and  $L_2$

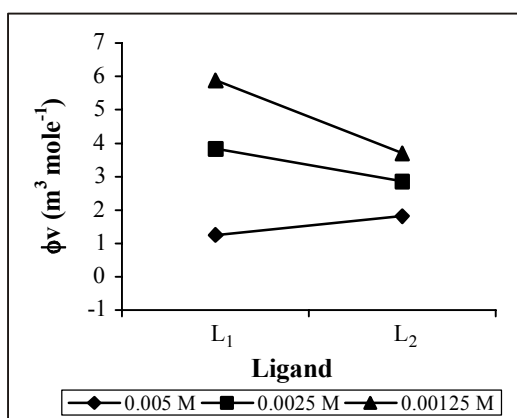


Fig. 3: Apparent molar volume of  $L_1$  and  $L_2$

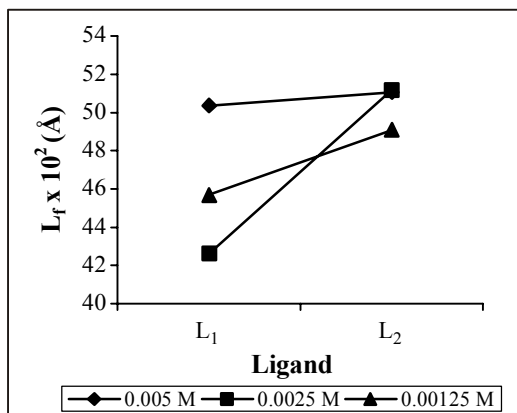


Fig. 4: Intermolecular free length of  $L_1$  and  $L_2$

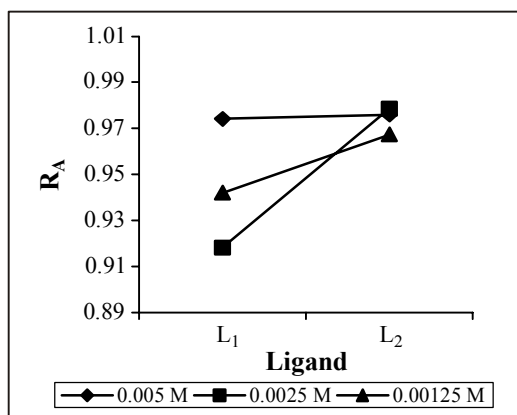


Fig. 5: Relative association of  $L_1$  and  $L_2$

### ACKNOWLEDGEMENT

The authors are very much thankful to Prof. V. D. Thakre, Head of Chemistry, G. V. I. S. H. Amravati for giving laboratory facilities. They are also thankful to Dr. S. B. Lohiya from Brijlal Biyani Mahavidyalaya, Amravati for their kind cooperation.

### REFERENCES

1. M. M. El-Bahay, M. C. El-Messal and A. D. El-Aal, J. Pure Appl. Ultrasonics, **21**, 103 (1999).
2. S. S. Aswale, S. R. Aswale, D. T. Tayade and P. B. Raghuvanshi, J. Pure Appl. Ultrasonic, **30**, 62 (2008).



3. M. G. Sheshagiri Rao, *Ind. J. Pure and Phy.*, **9**, 169 (1971).
4. R. P. Varma, Surendra Kumar, *Ind. J. Pure Appl. Phy.*, **38(2)**, 96 (2000).
5. S. S. Yadav, Y. P. Singh, Rajkumar, *Ind. J. Coun. Chem.*, **16(2)**, 20 (1992).
6. K. Sheshagiri and K. C. Reddy, *Acoustica*, **29**, 59 (1973).
7. A. Ali, K. Tiwari, A. K. Nain and V. Chakravartty, *Ind. J. Phy.*, Pt. B, **74(5)**, 351 (2000).
8. S. K. Upadhyay, *Ind. J. Chem.*, **39(5)**, 537 (2000).
9. S. Gnananba and B. R. Rao, *Ind. J. Pure & Appl. Phy.*, **7** (1969).
10. E. Baumgartner and G. Atkinson, *J. Zeit Fer, Phy, Chemie (Leipzig)*, **252**, 516 (1973).
11. J. D. Pandey, K. Mishra, A. Shukla and D. D. Rai, *Can. J. Chem.*, **65**, 303 (1987).
12. S. A. Ikhe and M. L. Narwade, *Indian J. Chem., Sect. A*, **44**, 1203 (2006).
13. S. D. Zade, *Rasayan J. Chem.*, **4(3)**, 620-629 (2011).
14. Christian T. Goralski and Bakthan Singara, *ARKIVOC*, (VII) 88-113 (2012).
15. P. S. Utale, P. B. Raghuvashi and A. G. Doshi, *Asian J. Chem.*, **10(3)**, 594 (1998).
16. A. I. Vogel, *Text Book of Practical Organic Chemistry*, 4<sup>th</sup> Ed. ELB Sand Longman, 264 (1978).
17. S. K. Ghosh, *Advanced General Organic Chemistry*, 1<sup>st</sup> Ed. New Central Book Agency, 1986, Reprinted (2003) p. 1033.
18. M. V. Kaulgud and S. S. Dhondge, *Ind. J. Chem.*, **27(4)**, 6 (1998).
19. H. Eyring and J. F. Kincaid, *J. Chem. Phy.*, **6**, 728 (1977).

*Revised : 29.01.2013*

*Accepted : 31.01.2013*