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Ultrasonic interferometric measurements of 2-hydroxy-5-chloro substituted chalcone dibromides in ethanol at 303 K

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ABSTRACT

Densities and ultrasonic velocities of substituted chalcone dibromides using 0.01 M concentration have been measured in ethanol at 303K. different acoustic properties like apparent molal volume, apparent molal compressibility, intermolecular free length, acoustic impedence have been determined. These properties were studied to solute-solute and solute-solvent interaction in solvent, which provide important and versatile information regarding internal structure, molecular association, complex formation and stability of complexes.

Keywords: 2-hydroxy-5-chloro substituted chalcone dibromides, interferometric measurements, acoustic properties, solute-solvent interaction.

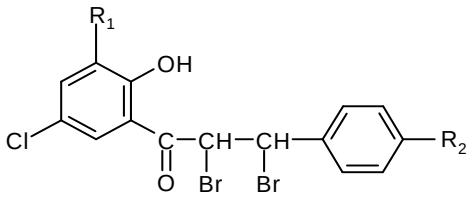
INTRODUCTION

Ultrasonic is the branch of acoustic, which consists of waves of high frequencies. Ultrasonic is the technique used for the study of molecular interaction inliquids. The study of molecular interaction in liquids provides valuable information regarding internal structure, molecular association, complex formation, internal pressure and stability of complexes[1]. Ultrasonic parameters are used extensively to study molecular interactions in pure liquids[2,3,4], liquid mixture[5,6] and electrolyte solution[7,8,9]. Aswale etal[10] investigated the comparative study of intermolecular interaction by acoustic properties of α-bromoacetophenones and cumaran-3-ones in ethanol and dioxan solvents. Acoustical studies on ternary mixture of toluene in cyclohexane and nitrobenzene at 308K[11]. Ultrasonic velocity and density of binary liquid mixture of diethyl ether with three non-polar solvents such as CCl4, CS2 and C6H6 at 303.15K[12].

In this present investigation, an attempt have been made to determine the densities and ultrasonic velocities of 2-hydroxy-5-chloro substituted chalcone dibromide viz. L_1, L_2, L_3 and L_4 in ethanol at 303K. The data obtained have been utilized to compute various acoustic properties for the study of various interactions.

MATERIALS AND METHODS

The chemicals and solvent used of A.R. grade to synthesized substituted chalcone dibromide as a ligand.
1. 2'-hydroxy-5'-chloro chalcone dibromide (L_1)
2. 2'-hydroxy-5'-chloro-4-methoxy chalcone dibromide (L_2)
3. 2'-hydroxy-3'-bromo-5'-chloro chalcone dibromide (L_3)
4. 2'-hydroxy-3'-bromo-5'-chloro-4-methoxy chalcone dibromide (L_4)



R_1 = -Br, -H

R_2 = -H, $-OCH_3$

These chalcone dibromides are synthesized by known method[13]. The solvent ethanol was purified by standard procedure[14]. Densities were measured with the help of bicapillary pyknometer (10.1 % kg m^{-3}). Pyknometer used of Borosil, 0.01M solution of ligand in ethanol solvent. weighing were made on Citizen CY 104 one pan digital balance (± 0.0001 gm). A special thermostatic arrangement was done for density and ultrasonic velocity measurements. Elite thermostatic bath was used, inwhich continuous stirring of water was carried out with the help of electric stirrer and temperature variation was maintained within ± 0.1 ^{0}C.

The speed of sound waves was obtained by using variable path,Single crystal interferometer (Mittal Enterprises, Model M-81S) with accuracy ± 0.03% and frequency 1 MHz was used in the present work. The densities and ultrasonic velocity of liquids in ethanol solvent at 303K. for the calculation of intermolecular free length the value of Jacobson's constant[15] (K = 631) at temperature 30 ^{0}C is used.

RESULTS AND DISCUSSION

In the present investigation measurement of densities and ultrasonic velocities of ligands L_1, L_2, L_3 and L_4 in ethanol has been carried out and given in Table No.1

Table No. 1: Acoustic parameters for ligands in ethanol at 303K
(Concentration: 0.01 M ; Frequency: 1 MHz)

Ligands	Us (m. sec^{-1})	ds x 10^3 ($kg.m^{-3}$)	βs x 10^{-10} (pa^{-1})	$ø_v$ (m^3mol^{-1})	$ø_k$ x 10^{-10} (m^3 mol^{-1} pa^{-1})	L_f x10^{-2} (m^{-1})	R_A	Z x 10^6 (kg m^{-2} sec^{-1})
L_1	1199.4	0.8772	7.9245	-9.5625	-168.794	1.7763	0.9960	1.0521
L_2	1146.9	0.8708	8.3030	-8.6856	-68.8925	1.8644	1.0572	0.9987
L_3	1196.9	0.8825	7.9098	-10.1610	-175.201	1.7747	0.9988	1.0563
L_4	1202.3	0.8865	7.8036	-10.6410	-191.048	1.7627	0.9928	1.0658

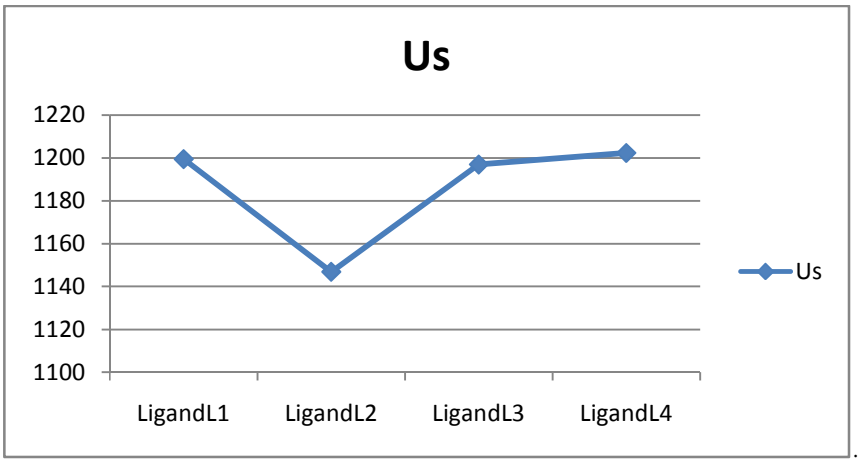


Fig. 1: Ultrasonic velocity of ligands L_1- L_4

Ultrasonic Velocity: (Us)
Ultrasonic velocity has been carried out for different the solutions. In ethanol at 303 K,

L_4 > L_1 > L_3 > L_2

Ligand L_4 have higher ultrasonic velocity due to presence of –Cl, –Br and –OH group. The presence of -Br atom which is bigger in size. -I effect of –Cl are acting on the ligand L_4 have highest dipole moment. Introduction of –OCH_3 group on second ring at para position affects the low velocity.

Density: (ds)
Density measurements have been carried out for different solutions. Density values of ethanol medium are lower. The order of density decreases in following order. In ethanol at 303 K,

$L_4 > L_3 > L_1 > L_2$

For ligands **L_1** to **L_4**. It is due to presence of –Cl, –Br,OH groups, these group show -I effect and +R effect of which latter predominates +R effect increases the electron density.

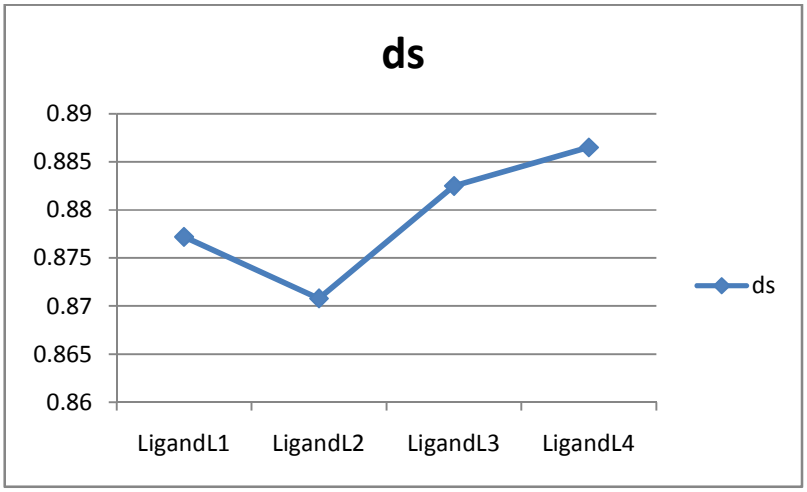


Fig. 2: Density of ligands L_1- L_4

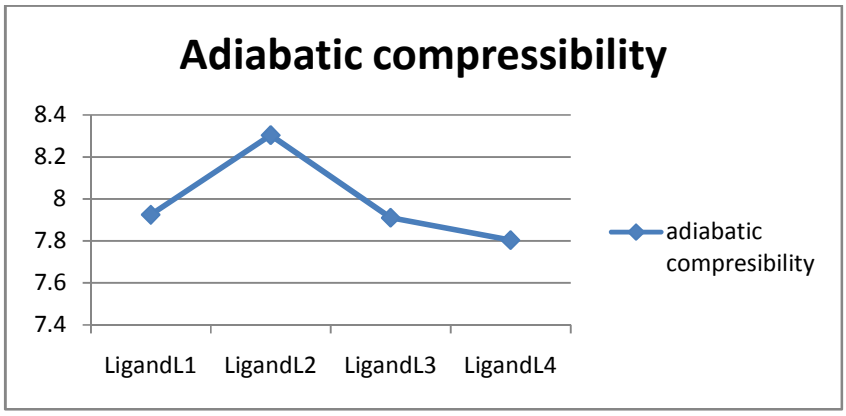


Fig. 3: Adiabatic compressibility of ligands L_1- L_4

Adiabatic compressibility: (βs)
Adiabatic compressibility is one of the important properties during the study of solute-solvent interactions and represented by β. In ethanol at 303 K,

$L_2 > L_1 > L_3 > L_4$

It is clearly observed that the β values in ethanol medium are considerably smaller, this may be due to nature of solvent. the parameters of solvents directly affect the values of β, with protic nature, polarity, high dielectric

constant and lower density of ethanol. In ethanolhydrogen bonding is also possible. The introduction of –Br, -OCH_3 group affects the β value .The adiabatic ompressibility may just explain the simple association or close packing or clinging of molecules.

Apparent molar volume: (φv)

Apparent molar volume is the thermodynamic property of solutions, which express the solute-solvent interactions, and it is obtained from the density and molarity of solution and the molecular weight of the solute. In ethanol at 303 K,

$L_2 > L_1 > L_3 > L_4$

It is observed that φv values are negative for all ligands in ethanol. Negative value obtained for ligand indicating the compactness of medium and after dissolution of solute due to the closer packing of molecules inside the shell more clinging is occurring. The negative values of φv for the system indicate the existence of smaller solute-solute interactions.

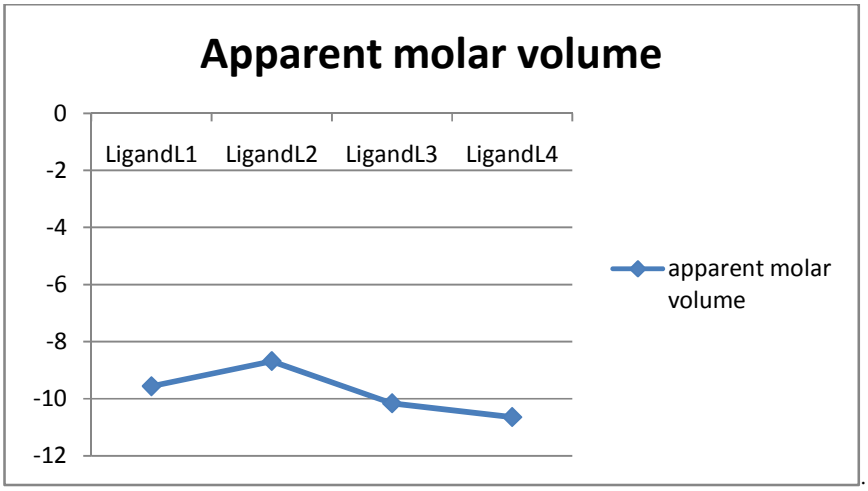


Fig. 4: Apparent molar volume of ligands L_1- L_4

Apparent molar compressibility: (φk)

Apparent molar compressibility (φk) is another important acoustic parameter, which explains the solute-solvent and solute-solute interactions in solutions. The structure of solute and the number of atoms present in it will have direct effect on φk values. It is observed that the φk values are negative for all ligands in ethanol. This interprets in terms of loss of compressibility of solute due to strong electrostatic solvation of ions. In ethanol at 303 K,

$L_2 > L_1 > L_3 > L_4$

The negative values of φk are indicative of ionic and hydro-phillic interactions in these systems. φk provides information regarding solute-solvent interactions. The appreciable negative values of φk for all of the system reinforce our earlier view about the existence of ion-solvent interactions.

Negative value of φk shows that interaction 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 looses its own compressibility to a certain extent.

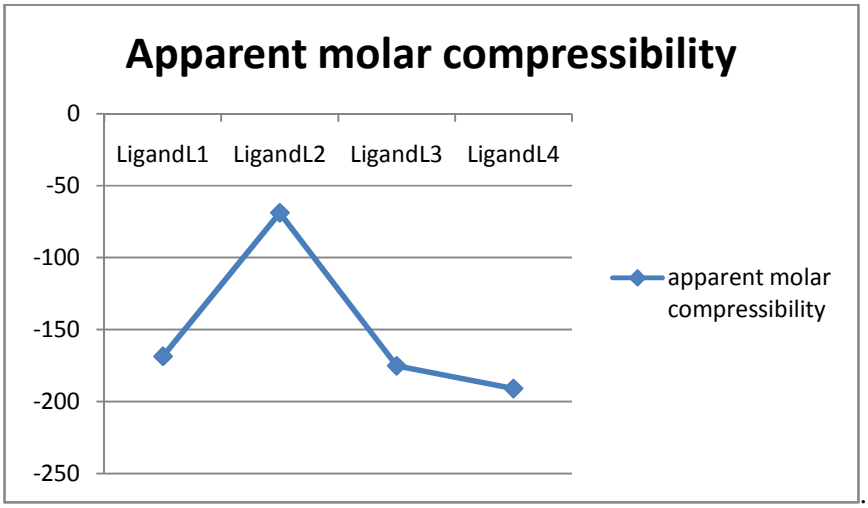


Fig. 5: Apparent molar compressibility of ligands L_1- L_4

Intermolecular free length: (L_f)
It is one of the important acoustic properties to study the intermolecular interactions. In ethanol at 303 K,

$L_2 > L_1 > L_3 > L_4$

The decrease in intermolecular free length values indicating that there is a significant interaction between solute and solvent molecules suggesting a structure promoting behaviour on the addition of solute.

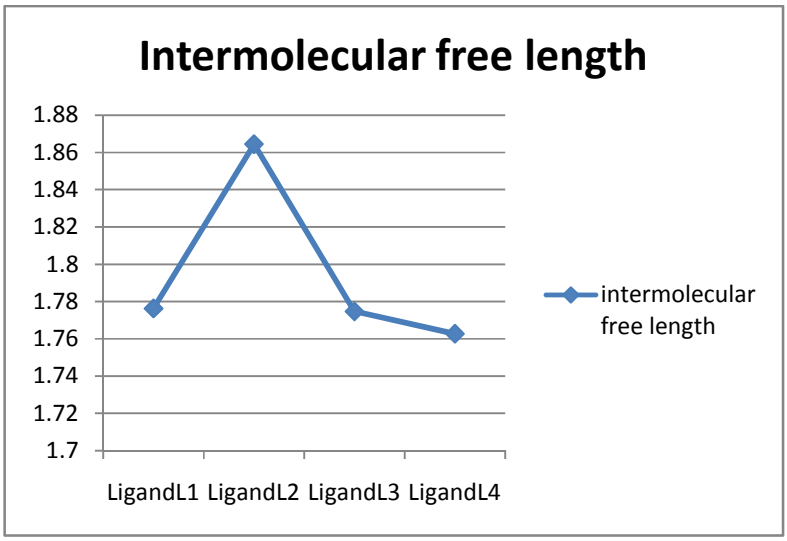


Fig. 6: Intermolecular free length of ligands L_1- L_4

The intermolecular free length depends upon the intermolecular attractive and repulsive forces. Lf is a predominating factor in determining the variation of ultrasonic velocity of solution. There is a significant interaction between solute and solvent molecules due to which its structural arrangement is also affected.

Relative association: (R_A)
Relative association is an acoustic property of understanding interaction, which is influenced 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. In ethanol at 303 K,

$L_2 > L_3 > L_1 > L_4$

Relative association affected due to the fact of different withdrawing substituents present in different ligands.

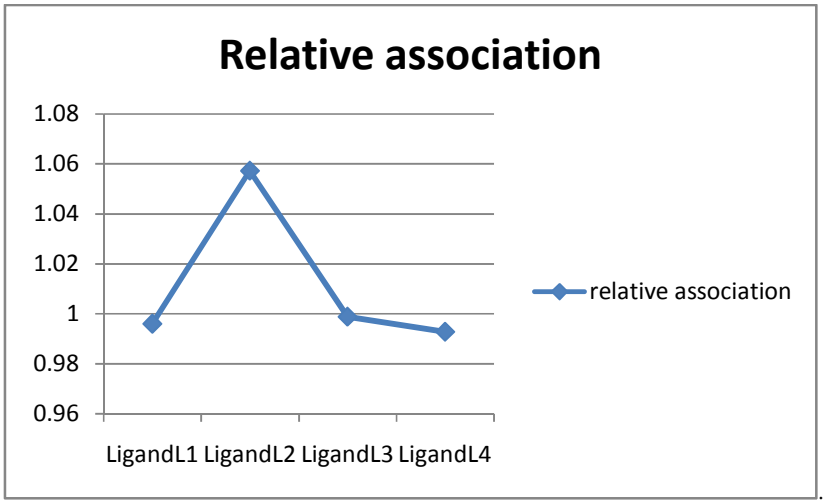


Fig. 7: Relative association of ligands L_1- L_4

Specific acoustic impedance: (Z)

Specific acoustic impedance is the complex ratio of the effective sound pressure at a point to the effective particle velocity at that point. In ethanol at 303 K,

$L_4 > L_3 > L_1 > L_2$

The values of z are continuously decreasing on changing the structure of ligand. The specific acoustic impedance depends upon the various structure of the liquid and the molecular packing in the medium.

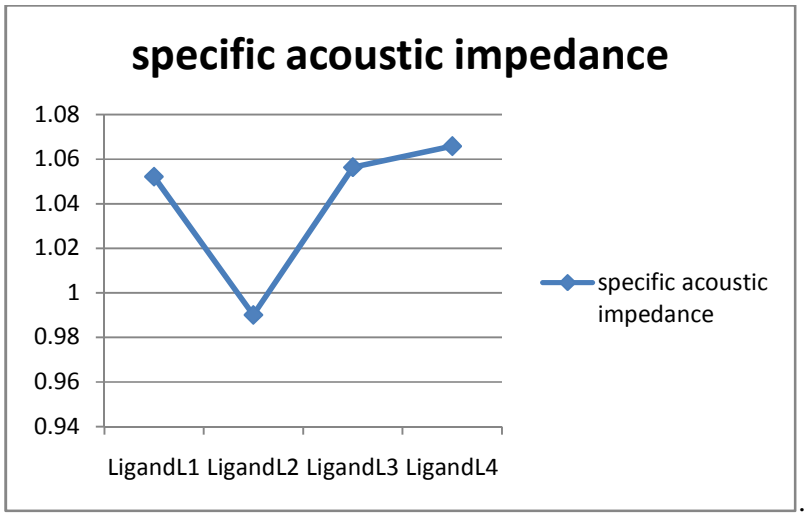


Fig. 8: Specific acoustic impedance of ligands L_1- L_4

CONCLUSION

By using ultrasonic interferometric study β, φv, φk, Lf, RA, z 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 synthesized ligands, which are used as solutes using ethanol solvent at 303 K in 0.01 M concentration.

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