Thermo acoustical molecular interaction study of azomethine and its Fe (III) metal complex using ultrasonic technique

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ABSTRACT

Ultrasonic velocity, viscosity and density of schiff base (E)–2-(2-chlorobenzylideneamino)benzoic acid and its metal complex of Fe(III) in DMSO have been measured at constant temperatures in the range of 306Kand different concentration. This schiff base was readily and conveniently accessible in high yields by green method. From the experimental data, the acoustical parameters such as adiabatic compressibility(β_s), relative association(R_A), specific acoustic impedance (Z), free path length (Lf), relaxation amplitude(α/f^2), relaxation time (τ), relative viscosity(ηr)and their excess values have been computed and presented as functions of compositions. The deviations from ideality of the acoustical parameters are explained on the basis of molecular interactions between the components of the mixtures. The variations of these parameters with composition of the mixture suggest the strength of molecular interactions in these mixtures.

Keywords: (E)–2-(2-chlorobenzyliden amino)benzoic acid, Fe(III) Metal complex, Ultrasonic velocity, Acoustical properties, Green chemistry.
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INTRODUCTION

In recent years, ultrasonic technique has become a powerful tool for studying the molecular behavior of liquid mixtures[1-3]. This is because of its ability of characterizing physico-chemical behaviour of liquidmedium[4-6].The measurement of ultrasonic velocity have been adequately employed in understanding themolecular interactions in liquid mixtures. Molecular interaction studies can be carried out by bothspectroscopic[7,8]and non–spectroscopic[9]techniques. However, ultrasonic velocity[10]and viscosity[11]measurements have been widely used in the field of interactions and structural aspect evaluation studies.

In the present study several acoustic parameters such asadiabatic compressibility(β_s), relative association(R_A), specific acoustic impedance (Z), free path length (Lf), relaxation amplitude(α/f^2), relaxation time (τ), relative viscosity(ηr)of (E)–2-(2-chlorobenzylidene amino)benzoic acid have beenreported using the experimental values of density, viscosity and ultrasonic velocity at constant temperatures 306K and different concentration.

In present day applications of ultrasonic are emerging in the field of forensic sciences, space research and also in wars. Ultrasonic waves are used in studying the properties of matter on the basis of interaction between the waves and constituents of the medium through which they pass. Determination of ultrasonic velocity and absorption coefficient has furnished methods for studying molecular and structural properties of liquids[12]. As there exists intimate relationship between ultrasonic velocity and chemical or structural characteristics of molecules of liquid,

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this gives a property of basic important to sound velocity in molecular theory of liquids. In the field of engineering and technology the ultrasonic waves are used for detection of flaws, testing of materials, mechanical cleaning of surfaces and also, the synthesis of schiff base is environmentally benign synthetic methods,which is eco-friendly and energy efficient greener methodogy.

Ultrasonic investigations of liquid mixtures consisting of polar and non polar components are of considerable importance in understanding intermolecular interactions between the component molecules and find applications in several industrial and technological processes[13-15].The variation of ultrasonic velocity and other ultrasonic parameters of binary liquid mixtures have been studied by many researchers and they have shed light upon structural changes associated with liquid mixtures of weakly or strongly interacting compounds[16-22].The study of molecular interaction in the liquid mixtures is also considerable in the elucidation of the structural properties of the molecules. The intermolecular interactions influence the structural arrangement along with the shape of the molecules.

In the present studies, the ultrasonic velocity and density in solutions of new schiff base and their metal complex of Fe(III)) have been measured and various acoustical parameters have been calculated in non-aqueous medium.In continuation of these investigations, the present study reports acoustical properties of schiff base in DMSO over different concentration range at 306K. The results are interpreted in terms of molecular interaction occurring in the solution.

THEORY
Acoustical properties:
The computation of ultrasonic properties require the measurements of ultrasonic velocity (U),viscosity (η) and density (ρ).

The densities of pure solvent and their solution of ligand and their metal complex were measured by using a single capillary pyknometer, made of borosil glass having a bulb capacity of 10 ml. The ultrasonic velocity of pure solvent and their solutionof ligand and their metal complex was measured by using single crystal variable path Ultrasonic Interferometer operating at 2 MHz. The accuracy of density and velocity are ±0.0001 g/cm3 and $\pm0.1\%$ cm/sec respectively. Viscosity was measured with the help of calibrated Ostwald's viscometer (Corning made) at $33 \pm 0.01°C$. Uncertainties in the measured viscosities were within $\pm 0.03\%$. Viscosity data were analysed using Jone's Dole equation and Vand's equation. All the measurements were carried out at 306K. The uncertainty of temperature is ± 0.1 K. From the experimental data of density, viscosity and ultrasound velocity of pure solvent and solutions, various acoustical parameters were calculated using following standard equations reported earlier.

1)ADIABATIC COMPRESSIBILITY (β_s)[23-24]
From the ultrasonic velocity(U)and density (d) the isentropic compressibility can be calculated from the following equation.

$$\beta_s = 1/(U^2 d) \quad , \quad \beta°_s = 1/(U_0^2 d_0)$$

2)RELATIVE ASSOCIATION (R_A)[26]
The relative association expressed in terms of density of solution (ds) and solvent (d_0) and also ultrasonic velocity of solution (Us) and solvent (U_0). The relative association calculated by the relation.

$$RA = ds / do (Uo / US)$$

3)SPECIFIC ACOUSTIC IMPENDENCE (Z)[26]
It is also determine the solvation of solute. It is expressed in terms of ultrasonic velocity of solution and density of solution. It is given by the formula.

$$Z = Us .ds$$

4)FREE PATH LENGTH (L_f)[26]
Free path length is responsible to determine the interaction between the ion and the solvent molecule. The free path length was calculated using the equation.

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$$L_f = \frac{M \times m}{V} \times \eta_r \times 293$$

5) RELAXATION AMPLITUDE[23,25]
The relaxation amplitude is expressed in terms of viscosity (η_s), density (ρ) and ultrasonic velocity of solution. It is denoted by (α/f^2) and measured in sec^2/m.

$$(\alpha/f^2) = \frac{8\pi^2 \eta_s}{3\rho U^2}$$

6) RELAXATION TIME[23,25]
The relaxation time is expressed in terms of viscosity (η_s), density (ρ) and ultrasonic velocity of solution. It is denoted by τ and measured in sec.

$$\tau = \frac{4\eta_s}{3\rho U^2}$$

7) RELATIVE VISCOSITY[26]
Relative viscosity (η_r) of various amino acids have been determined from density measurement and viscometric measurement using relation,

$$\eta_r = \frac{d_s \cdot t_s}{d_0 \cdot t_0}$$

EXPERIMENTAL SECTION

General procedure for the synthesis of Schiff base:-(E)–2-(2-chlorobenzylidene amino)benzoic acid.[27]
A mixture of 2-Chlorobenzaldehyde (0.5Mole) ,4-Aminobenzoic acid (0.5Mole) and (0.5 mL) of Lemon Juice was grinding at room temperature for 40 minutes. After completion of the reaction as indicated by TLC, the reaction mixture was poured on to crushed ice and stirred for 5-10 minutes. The solid separated was filtered under suction, washed with ice cold water and then recrystallized from ethanol.

2-chlorobenzaldehyde   4-amino benzoic acid   (E)-2-(2-chlorobenzylidene amino) benzoic acid
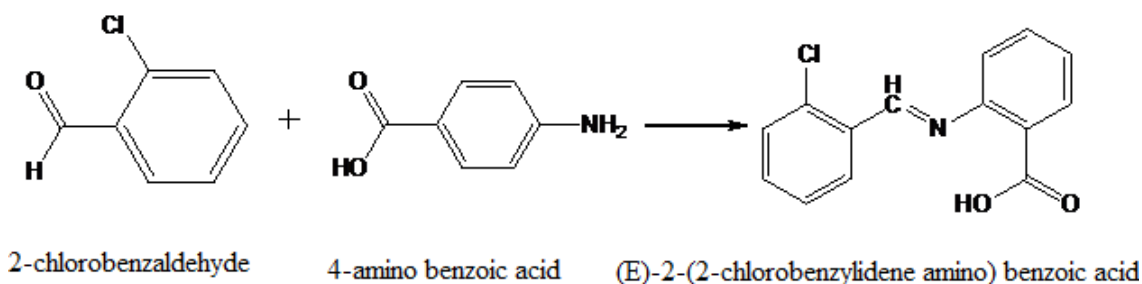
Metal complex was synthesized using 1:1 metal–ligand stoichiometric proportions. The metal complex was synthesized by mixing the DMSO solution of schiff base with the metal solution of different concentration i.e. 0.1M, 0.01M and 0.001M

RESULTS AND DISCUSSION

Due to the various types of applications of schiff base and their metal complex the research work in the field of co-ordination chemistry is increased and lot of work has been published on schiff base metal complex. Substituted aromatic aldehyde and its schiff base have shown considerable interest with regard to their chelating ability with the transition metal ions Fe(III) [28-29]. The chemistry of schiff base metal complex are of interest because these species display a variety of reactivity mode and also because they possess catalytic and biological activity[30].

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In the present work acoustic parameters such as, adiabatic compressibility (β_s), relative association (R_A), free length (L_f), acoustic impedance (z), relaxation amplitude (α/f^2) and relaxation time (τ) have been calculated for substituted schiff base and its metal complex at different concentrations. All these parameters are studied at constant temperature and at a different concentrations of solution.

Table No.1-Ultrasonic properties of Schiff Base and their Metal complexes in DMSO solvent at 306K

	Acoustic properties	Ultrasonic properties of Schiff Base in DMSO solvent at 306K			Ultrasonic properties of Schiff Base and Fe(III) complexes in DMSO solvent at 306K		
Sr. No.	Concentrations	0.1M	0.01M	0.001M	0.1M	0.01M	0.001M
1	Density (gm/cm3)	1.2759	1.2729	1.2751	1.2504	1.2430	1.2420
2	Viscosity (η)(m/s)	0.7910	0.7255	0.6885	0.8752	0.8203	0.7576
3	Ultrasonic Velocity (U)	1.5518	1.2572	1.1630	1.4568	1.2992	1.2589
4	Relative Association (R_A)	1.2019	1.2452	1.3870	1.2359	1.2935	1.2009
5	Adiabatic Compressibility (β_s)	0.7109	0.7905	0.8209	0.7431	0.7846	0.7997
6	Free path length (Lf) A^0	1222.84	112.16	10.643	2199.38	206.135	19.037
7	Specific acoustic impedance (Z) (m/sec.gm/cm3)	1.0473	1.0062	0.9064	0.9932	0.9848	0.9236
8	Relative viscosity (η r) (m/s)	1.6114	1.4780	1.4026	1.7830	1.6711	1.5433
9	Relaxation amplitude (α/f^2)	24.189	23.981	28.092	29.895	31.423	25.078
10	Relaxation Time (τ)	1.4245	1.2266	1.2161	1.5934	1.5160	1.2717

The interaction between substituent with solvent (DMSO) involves the association of anions and cations. The behavior of molecule is depends on the size, charge and concentration of electrolyte in the solution[31]. This interaction between schiff base and metal alsoschiff base and solvent can be followed by measuring the acoustic properties of the solution.The variation of different parameters with changing substituent of schiff bases have been calculated by using appropriate equations and are reported.

It is observed that viscosity increases with rise in concentration. This indicates that there exists a strong interaction between solute and solvent which is also supported by ultrasonic velocity. The variation of viscosity with concentration is as shown in table no-1. it is observed that adiabatic compressibility (β_s) decreases with increase in concentration of substituted schiff bases. Due to this it results in more cohesion, and lead to a decrease in (β_s). The decrease in (β_s) results in an increase in the value of ultrasonic velocity (U).

The free length (Lf) is another parameter which is calculated using ultrasonic velocity and adiabatic compressibility. It is observed that (Lf)decreases with the decrease in concentration of substituted schiff bases. Decrease in intermolecular free length leads to positive deviation in sound velocity and negative deviation in compressibility. This indicates that the molecules are nearer in the system. The values of intermolecular free length (L_f) are indicative of solute-solvent interaction and are in supports of the above observation.

Relative association(R_A)is the property used to understand the solute-solvent interaction.(R_A)is less in case of schiff base having ring deactivatingsubstituent.Ifschiff base nuclei has ring deactivating substituent then it has a less interaction with solvent molecule and hence has a greater free length. And finally relaxation amplitude and relaxation time is calculated for solutions of different concentration of schiff base and its metal complexe. Value of these quantity show system is stabilized in greater extent.

CONCLUSION

Ultrasonic velocity and density have been measured for organic solution of schiff bases and its metal complex of different concentrations at 2 MHz. The more value of viscosity and ultrasonic velocity indicated more is the concentration, and this shows solute-solvent interaction present in the solution.The existence of type of molecular interaction is solute-solvent is favored in system schiff base- solvent and schiff base-metal, confirmed from the U, ρ, η, βa, Lf, and R_A data.

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