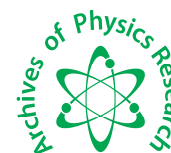




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### The Electronic Effect on the Inter and Intra Molecular Hydrogen Bonding in 5 Chloro Salicylaldehyde and Aniline in CCl<sub>4</sub> System

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#### ABSTRACT

The interaction between substituted carbonyl phenol with aniline in CCl<sub>4</sub> solvent and in liquid state is studied by various techniques. The results have been found in the order of magnitude as we had expected, but remarkable small differences have turned out between the interaction parameters of 5 chloro salicylaldehyde and aniline. The carbonyl absorption is quite sensitive to substitution, solvent effect and the introduction of a double bond in conjugation with the carbonyl group. An appreciable spectral change, on altering the substitution, indicates the formation of an intra and intermolecular hydrogen bond on the above system. The functional groups were identified from FTIR analysis. <sup>1</sup>H-NMR spectroscopic studies are employed to elucidate the structure of the title mixture. The molecular acoustics and the physico-chemical behavioural studies have been investigated by measuring ultrasonic velocities, density, viscosity and reflective index.

**Key words:** Hydrogen bonding, Steric and Electronic factors, Inductive and Mesomeric effect, Halogen, Substituent.

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#### INTRODUCTION

No field of science is so closely related with our daily activities as in organic chemistry, touches almost every phase of life [1]. Hydrogen bonds and the effects they have on the properties of compounds are important in various aspects of chemistry, biology and material science. The carbonyl groups or aromatic rings in the same molecule as the OH or NH group may cause similar shifts by intramolecular action [2]. Hydrogen bonding will influence not only the OH vibration frequency but also the C=O vibration to which it hydrogen bonds.

We choose salicylaldehyde a compound with well recognized significance in many branches of chemistry as an anti oxidant, fungicide, laticide and an important dye intermediate electron acceptor and aniline is the proto typical aromatic, electron donor group, and plays a vital role in the manufacturing of synthetic dyes, drugs and pesticides[3]. Chloro, a substituent halogen atom, often influences the vibrational frequencies of carbonyl groups by a through space interaction, which may be electrostatic or steric in nature. Because of the polarity of amino group in aniline and carbonyl group in 5 chloro salicylaldehyde, it forms intermolecular hydrogen bonding with solvent CCl<sub>4</sub> in solutions [4]. The newly formed mixture with optimum physical properties due to the hydrogen bonding is expected to find a special position in the organic chemistry which includes the synthesis of dyes, drugs and pesticides.

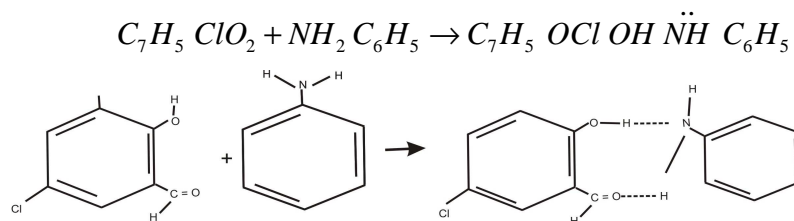
The purpose of the present research work is to summarize the spectral changes and the physico chemical behavioural changes which can be ascribed, with some degree of confidence, to intra molecular hydrogen bonding and to deduce from the data certain generalization concerning the inter and intramolecular hydrogen bonding in the title mixture.

## MATERIALS AND METHODS

### 2. Experimental Details

The commercially available 5 chloro salicylaldehyde and aniline with  $\text{CCl}_4$  (Merck quality) have been used to form the hydrogen bonding. The solute concentrations of 0.05M and 0.03M of the title mixture was prepared, and immediately the reaction began to take place between 5 chloro salicylaldehyde (electron acceptor) and aniline (electron donor) through hydrogen transfer.

The 5 chloro salicylaldehyde interacts with aniline through a single N-H-O hydrogen bond [5].



## RESULTS AND DISCUSSIONS

### 3.1 Spectral characterization of the title mixture

The recorded FTIR spectrum is shown in Figure.1. The functional groups and the formation of hydrogen bonding in the above title mixture have been identified by Bruker optics FTIR Spectrometer in the region  $400\text{-}4000\text{ cm}^{-1}$ . In the case of IR spectral data of the title mixture, normally the carbonyl mixture, the carbonyl stretching frequency in aryl aldehydes lies in the range  $1715\text{-}1695\text{ cm}^{-1}$ . In 5 chloro salicylaldehyde the carbonyl stretching frequency occurs at  $1613\text{ cm}^{-1}$  due to intra molecular hydrogen bonding. The lowering is caused by chelate type hydrogen bonding (intra molecular bonding)

The carbonyl stretching frequency in the title mixture of 5 chloro salicylaldehyde and aniline occurs at  $1716\text{ cm}^{-1}$  which proves the absence of intra molecular hydrogen bonding. In the mixture of 5 chloro salicylaldehyde and aniline, NH bending frequency of aniline group occurs at  $1358\text{ cm}^{-1}$  while in pure aniline it is between  $1650$  and  $1580\text{ cm}^{-1}$ . The lowering is caused by extensive intermolecular hydrogen bonding due to

- 1) Inter molecular hydrogen bonding between phenolic OH and nitrogen of aniline.
- 2) Carbonyl oxygen and amino hydrogen of aniline.
- 3) Phenolic oxygen and amino hydrogen of aniline.

There is a chelate ring formation consequent to this and hence the large decrease in the NH bending frequencies ( $1560\text{ cm}^{-1} - 1358\text{ cm}^{-1}$ ). All the above spectral data conform to the formation of the title mixture due to inter molecular hydrogen bonding.

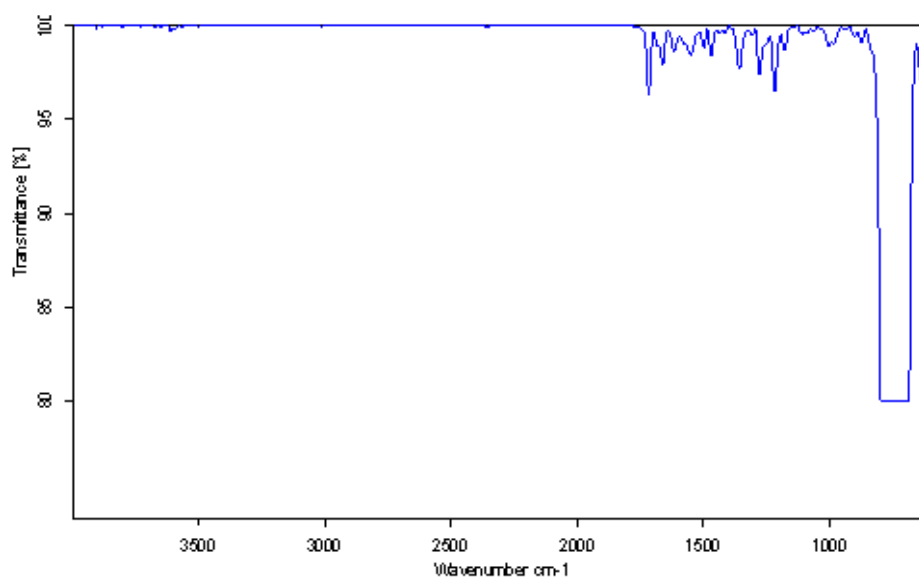


Figure.1 FTIR Spectrum of 5 – Chloro Salicylaldehyde with Aniline in  $\text{CCl}_4$  system.

The 300 MHz proton NMR spectrum of the title mixture measured in DMSO using Bruker instrument, is shown in figure 2. In the  $^1\text{H}$  - NMR spectrum of aniline a signal at 3.6ppm was corresponding to the amino hydrogen and 5 chloro salicylaldehyde has a signal at 10.9ppm corresponding to the phenolic proton; But in the 1:1 mixture of 5 chloro salicylaldehyde and aniline the phenolic proton of 5 chloro salicylaldehyde occurs at 14.2ppm. There is lot of increase in the ppm value which supports intermolecular hydrogen bonding involving chelate formation. Chelate ring formation causes deshield and hence absorption occurs at higher ppm value. Also the electrons associated with Cl atoms and C=O group exert long range shielding effects on the neighbouring protons. This effect depends very much on the relative steric disposition of the two interacting systems. All these spectral data indicate that the title mixture was formed under experimental condition.

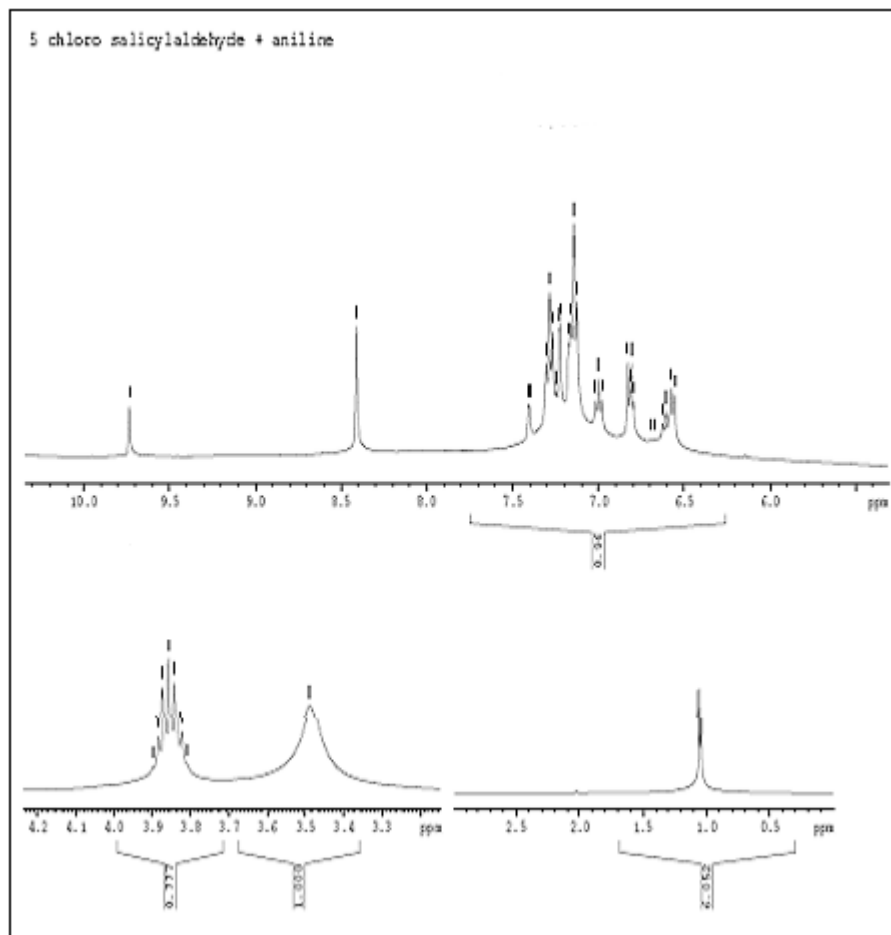


Figure.2  $^1\text{H}$ - NMR spectrum of 5-Chloro Salicylaldehyde with Aniline in  $\text{CCl}_4$  system.

### 3.2. Molecular acoustics and physico chemical behavioural studies

The molecular association between the title mixture (5chloro salicylaldehyde and aniline) has been investigated by measuring ultrasonic velocity, viscosity, refractive index and density at 303 k with different mole fractions in  $\text{CCl}_4$  solution and various acoustical parameters are also evaluated. The ultrasonic velocity was measured using a single crystal ultrasonic interferometer with an operating frequency of 2MHZ, supplied by M/S Mittal Enterprises, New Delhi.

In this report we have evaluated the acoustic parameters namely the adiabatic compressibility ( $\beta$ ), free length ( $L_f$ ), free volume ( $V_f$ ), internal pressure ( $\pi_i$ ), relaxation time ( $\tau$ ), acoustic impedance ( $z$ ) and cohesive energy ( $C_e$ ) for the title mixture. The results are discussed in terms of molecular interactions [9]. The molecular associations increase ultrasonic velocity ( $U$ ), adiabatic impedance ( $Z$ ), free length ( $L_f$ ), relaxation time ( $\tau$ ) and free volume ( $V_f$ ), and decrease the internal pressure ( $\pi_i$ ), adiabatic compressibility ( $\beta$ ) and cohesive energy ( $C_e$ ) [10].

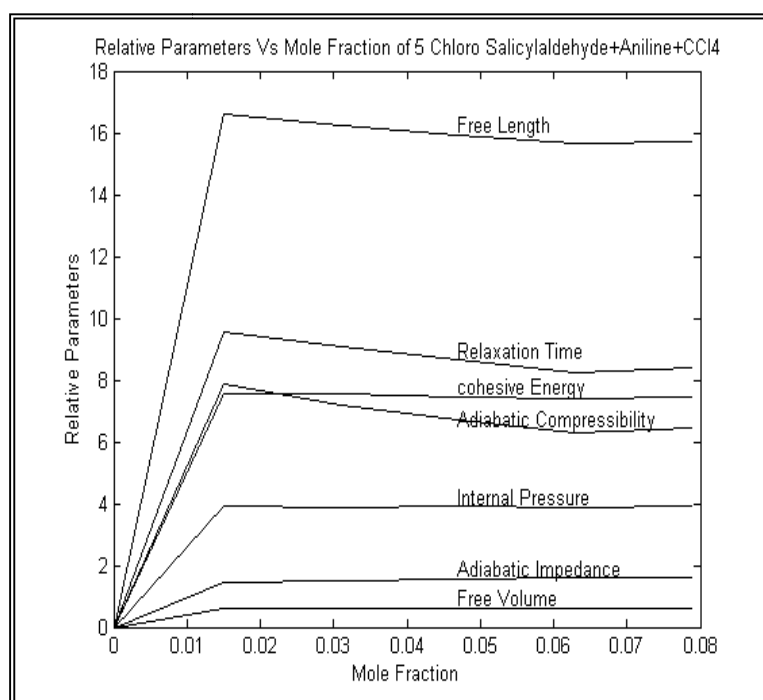
These result strengthen the strong molecular association between the unlike molecules of the title mixture through hydrogen bonding [11]. The experimental values are listed in Table.1 and the parameters are listed in Table 2.

**Table.1 Mole fractions of 5 Chloro Salicylaldehyde( $X_1$ ), mole fractions of aniline( $X_2$ ) and values of ultrasonic velocity (U), density ( $\rho$ ) viscosity ( $\eta$ )and refractive index (D) of 5 chloro salicylaldehyde + aniline +  $CCl_4$** 

$X_1$	$X_2$	$U\text{ms}^{-1}$	$\rho\text{kgm}^{-3}$	$\eta \times 10^3$ $\text{Nsm}^2$	D
.01	.005	894	1.5929	0.0009128	1.4877
.02	.011	932	1.5970	0.0009423	1.4878
.03	.017	958	1.6180	0.000963	1.4896
.04	.023	990	1.6250	0.000986	1.4980
.05	.029	971	1.6410	0.000977	1.4875

**Table-2 Mole fractions of 5 Chloro Salicylaldehyde( $X_1$ ), mole fractions of aniline( $X_2$ ) and values of adiabatic compressibility ( $\beta$ ) cohesive energy (Ce) free length (Lf), relaxation time ( $\tau$ ), internal pressure ( $\pi$ ) adiabatic impedance (Z), free volume ( $V_f$ ) of 5 Chloro Salicylaldehyde + Aniline +  $CCl_4$** 

$X_1$	$X_2$	$\beta \times 10^{-10}$ $(\text{M}^2 \text{N}^{-1})$	$(C_e \times 10^6)$ $\text{kJmol}^{-1}$	$L_f \times 10^{-10}\text{m}$	$\tau \times 10^{-12}\text{S}$	$\pi_i \times 10^6$ $(\text{Nm}^{-2})$	$Z \times 10^6$ $\text{kgm}^2\text{S}^{-1}$	$V_f \times 10^{-7}$ $\text{m}^3\text{mol}^{-1}$
.01	.005	7.85926	7573.93	16.6311	0.95650	3.9109	1.4232	0.5930
.02	.011	7.20880	7526.93	16.2630	0.90570	3.8859	1.4884	0.6043
.03	.017	6.73420	7469.16	15.9364	0.86460	3.8961	1.5500	0.6121
.04	.023	6.27870	7420.61	15.6429	0.82540	3.8769	1.6087	0.6232
.05	.029	6.46320	7430.92	15.7180	0.84194	3.9100	1.5934	0.6162

**Figure.3 Free length, cohesive energy, adiabatic compressibility, internal pressure, adiabatic impedance, relaxation time and free volume vs mole fraction of 5 chloro salicylaldehyde + aniline+  $CCl_4$** 

### 3.3 Density Measurement

The density was measured by a 10 ml specific gravity bottle calibrated with double distilled water and acetone. In the present study density increases as the molar concentration of the solute increases. So the density values are often higher compared to that of the parent aldehydes. It shows the existence of strong intermolecular attractions and the formation of hydrogen bonding reflected as the higher density[12].

### 3.4. Viscosity measurement

The viscosity of the pure liquids and liquid mixtures are measured using an Ostwald's viscometer calibrated with double distilled water. The time of flow is measured using a racer stop watch with an accuracy of 0.1.sec. In the present study of the title mixture, the viscosity increases as the molar concentration of the solute increases [13]. A

dip at 0.05 mole fraction of 5 chloro salicylaldehyde and 0.029 mole fraction of aniline in viscosity variation indicates that the structure formation may be in equilibrium whereas at other mole fractions the predominantly existing molecule may affect the other.

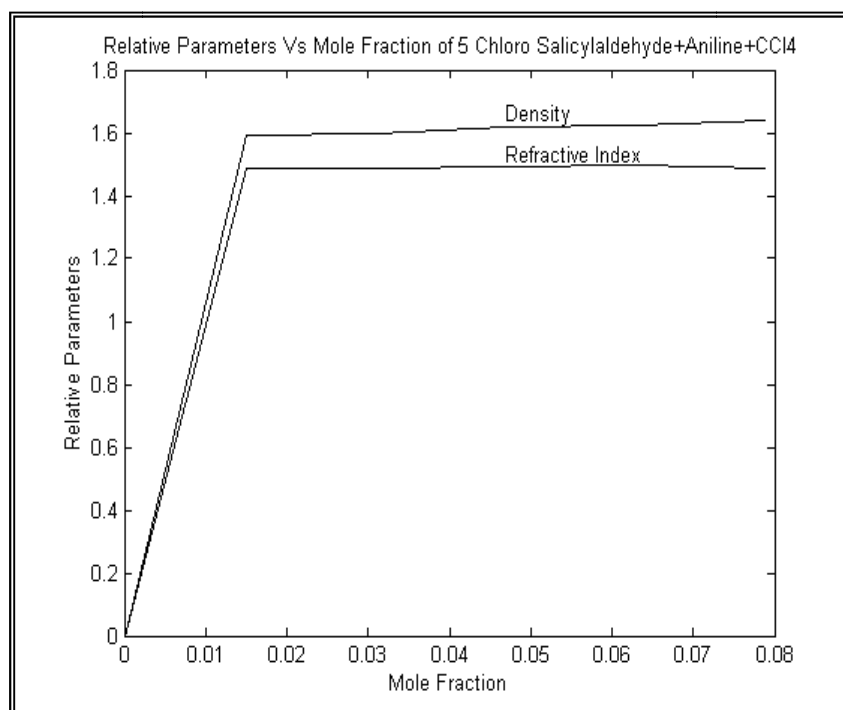


Figure.4 Density and refractive index vs mole fraction of 5 chloro salicylaldehyde + aniline+ CCl<sub>4</sub>

### 3.5 Refractive index measurement

Refractive indices are measured with an Abbe refractometer (Erma, A302A) and the values are obtained for Na-D-light with an error less than  $\pm 0.0002$  units. The refractive index of the title mixture increases with its density. However, there does not exist an overall linear relation between the refractive index and the density for all the mole fraction of the title mixture. A dip at 0.05 mole fraction of 5 chloro salicylaldehyde and 0.029 mole fraction of aniline, the refractive index decreases and the density increases [14]. So the refractive indices are also often higher compared to the parent aldehydes. It shows the strong formation of hydrogen bonding in the title mixture.

### CONCLUSION

A strong hydrogen bond exists between the title mixture through O-H - N and a strong molecular interaction between the unlike molecules. It is inferred that the relative strength in intermolecular interactions depend upon the presence of electron donor and electron acceptor groups. A qualitative interpretation of the correlation between the different substituent has effects on the IR absorption observed for each of carbonyl stretching vibration and amino group. The carbonyl stretching vibration is altered, presumably the formation of the intermolecular hydrogen bond or related interaction. The steric and mesomeric effects, introduced by substituent, may influence the strength of the inter molecular H bond significantly.

The presence of protons has been confirmed from the <sup>1</sup>H-NMR analysis. The strong molecular association between the unlike molecules of the title mixture through hydrogen bonding has been confirmed by molecular acoustic studies. The measurement of physical properties like density, viscosity and refractive index shows the strong intermolecular attractions between the title mixture.

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