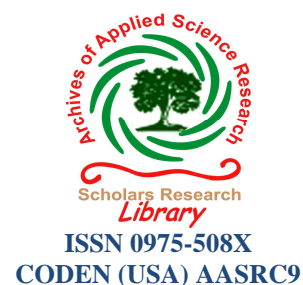




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## Analysis of O...H...N and N...O...H intermolecular interaction involving nitro in substituted 5-nitro salicylaldehyde and aniline

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### ABSTRACT

Two intermolecular interactions of (1) hydrogen bond and (2) substitution effect were analyzed and compared, besides the investigation of intermolecular interactions between the two polar molecules forming the solution in a non polar solvent. For this purpose the FTIR and  $^1\text{H}$ -NMR spectroscopic methods were used. The molecular acoustics provides information about the molecular behaviour of liquids owing to its ability of characterizing physico chemical behaviour of the medium. The results obtained allowed us to show that substituents ( $\text{NO}_2$ ) in the para or the ortho position with respect to either OH or CHO in H-bonded systems which interact more strongly than the other systems. The substituent effect, due to the intermolecular charge transfer from the ortho-counter substituent ( $\text{NO}_2$ ) to the proton donating group (OH), is greater than for the interaction of para-OH with the proton-acceptor group (CHO).

**Keywords:** Hydrogen bonding, Solute-Solute interaction, Physico chemical behaviour, Intra and Intermolecular bonding.

### INTRODUCTION

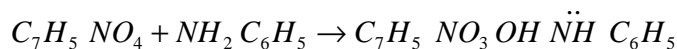
The study of hydrogen bonding has been made in the liquid systems by FTIR spectroscopy, Nuclear magnetic resonance, and molecular acoustics studies. The complex formation of 5 nitro salicylaldehyde, a proton acceptor with aniline, a proton donor, has confirmed the existence of the formation of 1:1 complexes in the above system[1]. salicylaldehyde is extensively used in the perfumery industry both as ingredient of cosmetics and pomads and also as fungicide, lavicide and ultraviolet stabilizer for polystyrene and as an important dye-intermediate. Aniline play a vital role in the manufacture of synthetic dyes, drugs and pesticide. Keeping both industrial and scientific interests in mind, an attempt has been made in the present work to study the hydrogen bonding between the carbonyl group of 5 nitro salicylaldehyde and the amino group aniline. One can use the theoretical principles to explain many of the frequency shifts that occur in vibrations when the substituent is altered[2]. The inductive and resonance effects are seen to be at work, together with an occasional through space influence or field effect. The present studies are concerned with the effect of the competitive intermolecular hydrogen bonding upon the position and intensity of the carbonyl-amino stretching absorptions in the substituted salicylaldehyde.[3]

The study also investigate how the substituent effect acts on  $\pi$  electron delocalization and H-bond strength in the case of aromatic systems with intermolecular H-bonding. Another revelation is, as a result of intermolecular H-bond formation, the proton donating group increases its electron donating power, and the proton accepting group increases its electron accepting power[4].

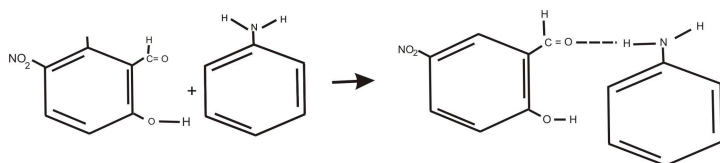
## MATERIALS AND METHODS

## EXPERIMENTAL DETAILS

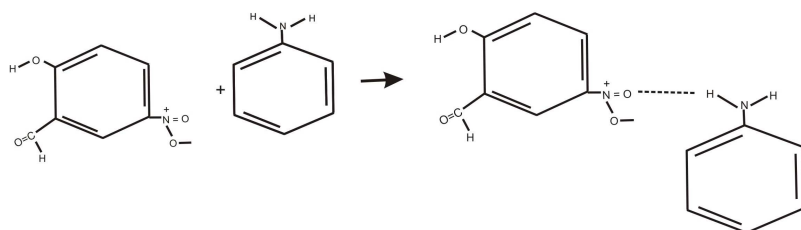
The solutions were prepared at the concentration of .05m / .037m in 5ml CCl<sub>4</sub>. The pure sample of 5-nitro salicylaldehyde, aniline and CCl<sub>4</sub> were of Merck quality.



I



II



The 5-nitro salicylaldehyde interacts with aniline through N---H---O and O---H---N hydrogen bonds.

## RESULTS AND DISCUSSION

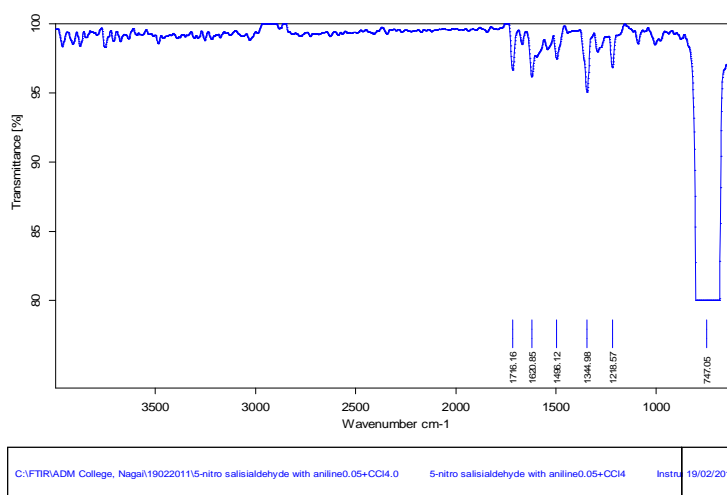
## 3.3 Spectral characterization of the title mixture.

The functional groups in the 5-nitro salicylaldehyde with aniline mixture have been identified by Burker optics FTIR spectrometer in the region 400- 4000cm<sup>-1</sup>. The FTIR spectrum of title mixture is shown in fig1. Normally in aryl aldehydes the carbonyl stretching frequency lies in the range of 1715-1695 cm<sup>-1</sup>. In 5-nitro salicylaldehyde the carbonyl stretching frequency occurs at 1631cm<sup>-1</sup> due to intramolecular hydrogen bonding. The lowering is caused by chelate type hydrogen bonding.

The carbonyl stretching frequency in the mixture of 5-nitro salicylaldehyde and aniline occurs at 1716cm<sup>-1</sup> which proves the absence of intramolecular hydrogen bonding. In the title mixture NH bending frequency of amino group occurs at 1344cm<sup>-1</sup> while in pure aniline it is in the range of 1650-1580cm<sup>-1</sup>. The lowering is caused by extensive intermolecular hydrogen bonding because of the following factors.

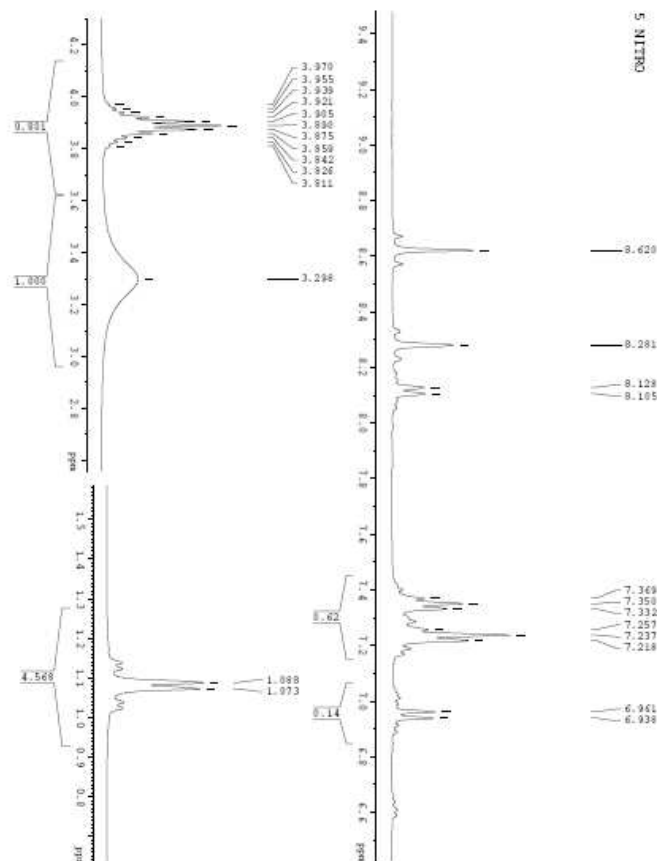
1. Inter molecular hydrogen bonding between phenolic OH and nitrogen of aniline.
2. carbonyl oxygen and amino hydrogen of aniline.
3. Nitro oxygen and amino hydrogen of aniline.
4. Phenolic oxygen and amino hydrogen of aniline

There is a chelate ring formation consequent to this and hence the large decrease in the NH bending frequencies (1560cm<sup>-1</sup> -1344cm<sup>-1</sup>) [5].

Figure -1 FTIR Spectrum of 5-nitro salicylaldehyde with aniline in CCl<sub>4</sub> system

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The 300 MHZ proton NMR spectrum of the title mixture measured using Bruker instrument is shown in figure 2.

Figure -2 <sup>1</sup>H- NMR spectrum of 5- nitro salicylaldehyde with aniline in CCl<sub>4</sub> system.

In the <sup>1</sup>H – NMR spectrum of the title mixture, the peak at 8.62 ppm strongly endures the formation of intermolecular hydrogen bonding. As a result, normally the phenolic OH group absorbs at 4.5 ppm. But in the title mixture due to intermolecular hydrogen bonding it is raised to a higher value around 9ppm.

Since the frequency shift for 5-nitro salicylaldehyde occurs at higher frequency the key atom in these substituent is bonded to another highly electronegative atom by a double bond. The electro negative atom pulls the electron pair of the multiple charge on the key atom. The key atom, in turn, withdraws electron from the benzene ring causing resonance [6].

### 3.3.3 Physico chemical behavioural studies and Molecular acoustics.

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.

The above studies reveal the valuable information about the complex formation between the above title mixture. The observed values are given in table.1

**Table-1 Mole fraction of 5- nitro salicylaldehyde (  $X_1$ ), mole fraction of aniline ( $X_2$ ) and values of Ultra sonic Velocity (U), Density ( $\rho$ ) Viscosity ( $\eta$ ) and Refractive Index (d) of 5-nitro salicylaldehyde + aniline +  $\text{CCl}_4$**

$X_1$	$X_2$	$U \text{ m s}^{-1}$	$\rho \text{ kg m}^{-3}$	$\eta \times 10^3 \text{ N s m}^{-2}$	d
0.01	0.005	976	1.5850	0.0009172	1.4980
0.02	0.011	1147.5	1.5919	0.0009483	1.4981
0.03	0.016	983.5	1.6180	0.0000973	1.5004
0.04	0.022	1043	1.6237	0.0011050	1.5009
0.05	0.027	997.7	1.6413	0.0013960	1.4876

Acoustic impedance (z) of a material is the opposition exerted by the medium to the displacement of the medium particles by the sound energy. Studies have shown that in solvent mixtures, when molecular interaction occurs, acoustic impedance exhibits a non-linear variation with increasing mole fraction of solute [7], which make the measurement of acoustic impedance important. It has been found that the acoustic impedance gives a peak in conjunction with ultrasonic velocity maxima and isentropic compressibility minima [8].

**Table-2 Mole fraction of 5-nitro salicylaldehyde ( $X_1$ ), Mole fraction 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- nitro salicylaldehyde + aniline +  $\text{CCl}_4$**

$X_1$	$X_2$	$\beta \times 10^{-10} \text{ (m}^2 \text{ n}^{-1})$	$(\text{Ce} \times 10^6) \text{ kJ mol}^{-1}$	$\text{Lf} \times 10^{-10} \text{ m}$	$\tau \times 10^{-12} \text{ s}$	$\pi \times 10^6 \text{ (nm}^{-2})$	$Z \times 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$	$V_f \times 10^{-7} \text{ m}^3 \text{ mol}^{-1}$
0.01	0.005	6.6232	7278.43	15.9523	0.8099	3.7393	1.5469	0.6717
0.02	0.011	4.7733	6812.03	14.6892	0.6035	3.5049	1.8256	0.8180
0.03	0.016	6.3895	7409.53	15.7284	0.8289	3.8639	1.5913	0.6272
0.04	0.022	5.6638	7652.83	15.2497	0.8344	3.9936	1.6927	0.5684
0.05	0.027	6.1219	8761.66	15.5063	1.1395	4.6088	1.6372	0.3760

In the present title mixture the ultrasonic velocity (u) increased and the intermolecular free length (Lf) as well as the adiabatic compressibility ( $\beta$ ) decreased. It shows that the intermolecular hydrogen bonding and the association is stronger. Similar results were obtained by earlier works in their liquid mixtures[9].

The variation of free volume ( $V_f$ ) and internal pressure ( $\pi$ ) with mole fraction are given in Table 2. It is observed that free volume ( $V_f$ ) decreases whereas the internal pressure ( $\pi$ ) increases that show the increasing magnitude of interaction. The cohesive energy (Ce) and the relaxation time ( $\tau$ ) increase in the title mixture [10].

### 3.3.4 Density, Viscosity and Refractive Index measurements.

The Density was measured by a 10ml specific gravity bottle calibrated with double distilled water and acetone. An Ostwald's viscometer was used for viscosity measurements. Refractive indices were measured with an Abbe's refractometer (Erma, A-802A) and the values were obtained for Na-D-light with an error less than  $\pm 0.0002$  units.

In the present study the existence of strong intermolecular attractions will be reflected as the higher density, viscosity and refractive index. The viscosity increases as the molar concentration of the solute increases. The density and viscosity show an increasing tendency whereas refractive index shows a decreasing nature initially and forms a dip at 0.04 mole fraction of 5-nitro salicylaldehyde and 0.022 mole fraction of aniline of the title mixture.

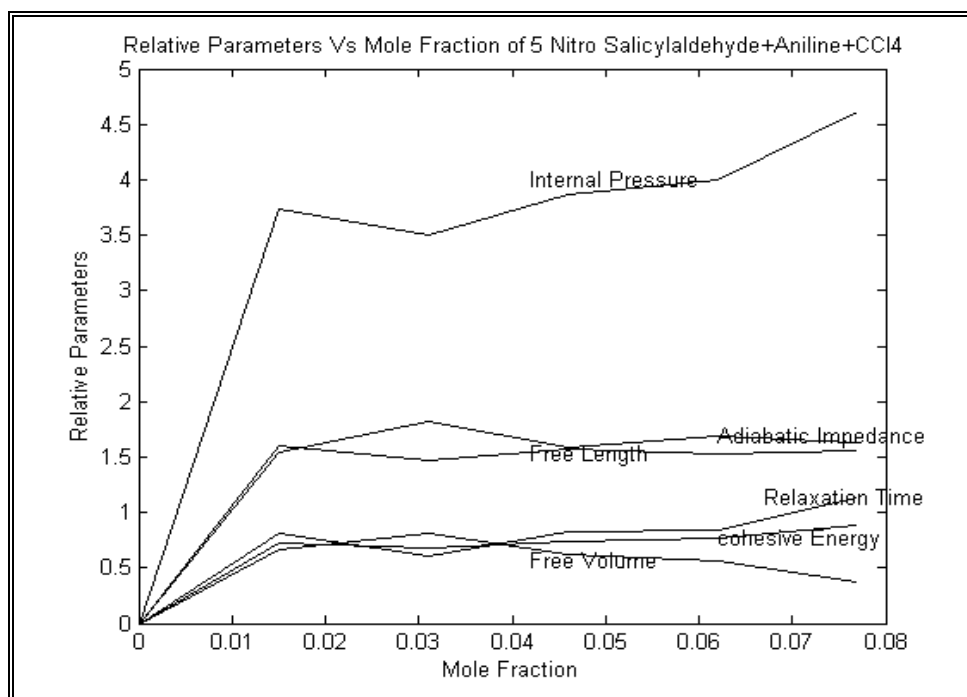


Figure - 3 Graph between Free Length, Cohesive Energy, Internal Pressure, Adiabatic Impedance, Relaxation Time and Free Volume Vs Mole Fraction of 5-nitro salicylaldehyde + aniline+ CCl<sub>4</sub>

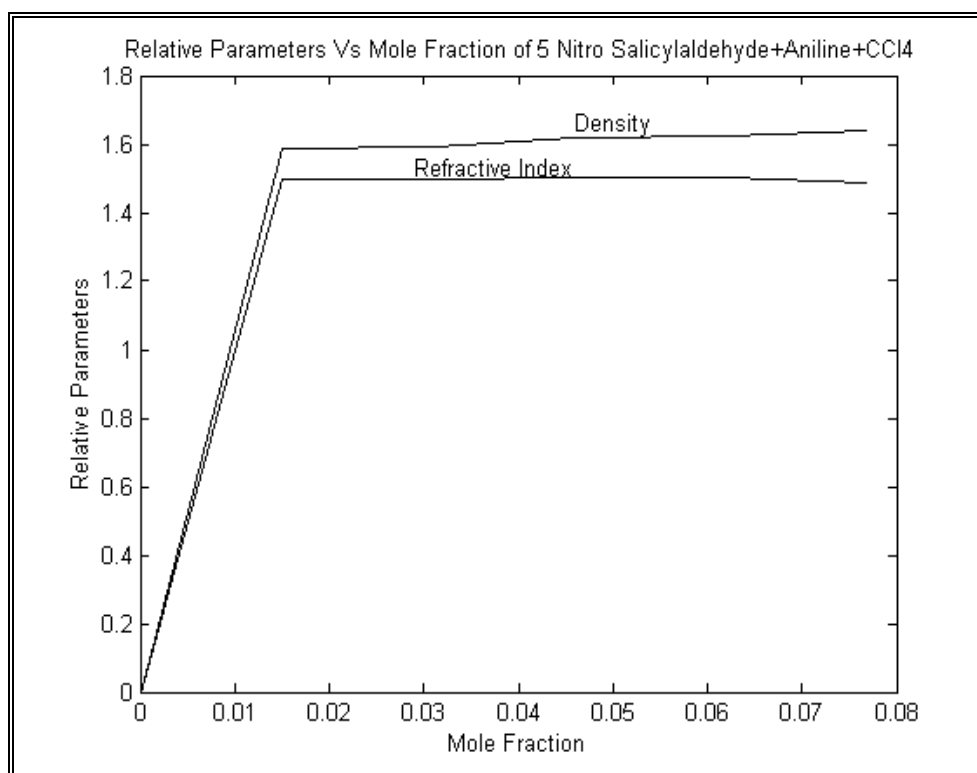


Figure - 4 Graph between Density and Refractive index Vs Mole fraction of 5 nitro salicylaldehyde + aniline+ CCl<sub>4</sub>

Owing to the addition of aniline to the mixture, increases the extent of intermolecular interactions existing in the system and thus density and viscosity show an increasing trend. However, for the viscosity variations, the molecular size is also an important parameter. Even though aniline possesses a ring structure, the NH<sub>2</sub> group attached with carbon atom of ring sufficiently increases the size of aniline molecule. Salicylaldehyde also possesses a ring structure; the NO<sub>2</sub> group attached with carbon atom of ring sufficiently increases the size of the solute molecule. Thus the viscosity of the title mixture increases [11].

### CONCLUSION

From the study one may conclude that the intermolecular (N-H...O, N-O...H...N) bonds and intramolecular (OH, CHO) bonds are formed between the title mixture. Owing to the effect of nitro group, the ortho hydrogen and the para carbon shifted the ortho hydrogen to downfield and the para carbon to upfield. The computed acoustical parameters and their values point to the presence of specific molecular interaction in the mixture. Hence it is concluded that the association in these mixtures is the result of inter and intramolecular hydrogen bonding in the title mixture. All the spectral data of IR and <sup>1</sup>H-NMR analysis indicate the complex formation between the title mixture.

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