Studies on Molecular Interaction in Bromo Substituent Salicylaldehyde with Aniline

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Abstract: ***Information concerning intermolecular hydrogen bonding in 5- bromo salicylaldehyde and aniline can be obtained by a variety of methods. Bromo salicylaldehyde is chosen in preference to other halogens as it is easily prepared and gives a strong intermolecular hydrogen bond. The effect of the aromatic ring substituent upon the frequency of the carbonyl in the title mixture has been examined by the FTIR spectroscopy and the 1H -NMR spectroscopic studies which are employed to elucidate the structure of the title mixture. The existence of strong intermolecular attraction will be reflected in molecular acoustics and physico chemical behavioral studies. The results are discussed in terms of the influence of steric and electronic factors and compared with other data in the literature.***

Keywords: Inter-Intra molecular bonding, FTIR, Molecular acoustics, Halogens, Steric and Electronic factors.

1. Introduction

Several studies are concerned with the bonded and non bonded carbonyl absorptions and the results are used to calculate the energy and relative strengths of the hydrogen bond involved [1]. The influence of other factors has, however, drawn little attention and the present studies are concerned with the influence of steric and electronic effects, competitive inter molecular hydrogen bonding upon the position and intensity of the carbonyl stretching absorption of the title mixture [2].

Such studies may well have biological implications like antibacterial, anti fungal and anthelmintic agents. It has been observed that the introduction of the substituent into the 5th position of salicylaldehyde lowers antifungal activity [3].

Resonance and intermolecular effects cause shifts in group frequency position. However the shifts in themselves are highly characteristic and so are useful for diagnostic purposes. [4, 5].The techniques of molecular acoustics are employed because they permit the equilibria present in the liquids to be investigated and they are also used to examine kinetic behavior and the visco elastic properties of the title mixture [6, 7].

2. Experimental details

The solute concentration of 0.05m and 0.029m of 5-bromo salicylaldehyde with aniline in CCl4 was prepared. All the specimens were (Merk quality) from our private collection.

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

$$C_7H_5\ BrO_2 + NH_2C_6H_5 \rightarrow C_7H_5\ OBrOH\ \ddot{N}H\ \ C_6H_5$$

3. Results and Discussion

3.1 Spectral characterization of the title mixture

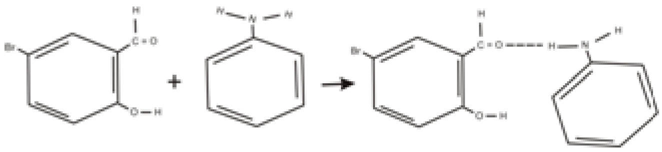
The 300 MHZ proton NMR spectrum of the title mixture measured using Bruker instrument is shown in figure 1. In the 1H-NMR spectrum of the title mixture, peaks at 8.35 ppm and 8.62 ppm strongly endure the formation of intermolecular hydrogen bonding. This is because the normal range of phenolic OH group absorbs at 4.5ppm. But in the title mixture, due to intermolecular hydrogen bonding, it is raised to a higher value around 9ppm. The electrons associated with Br atoms and C=O group exert long range shielding effects on neighboring 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 [8].

In the case of IR spectral data of the title mixture, the recorded FTIR spectrum is shown in Figure 2. The solutions were scanned from 400 cm-1 to 4000 cm-1. The spectrum was measured with a Bruker optics FTIR spectrometer. Normally in aryl aldehydes the carbonyl stretching frequency lies in the range 1715-1695 cm-1. In 5-bromo salichylaldehyde the carbonyl strectching frequency occurs at 1623cm-1 due to intra molecular hydrogen bonding. The lowering is caused by chelate type hydrogen bonding.

The carbonyl stretching frequency in the title mixture occurs at 1718cm-1 which proves the absence of intra molecular hydrogen bonding. In the mixture of 5-bromo salicylaldehyde and aniline, NH bending frequency of amino group occurs at 1498cm-1 while in pure aniline it is in the range of 1650-1560cm-1. The lowering is caused by extensive intermolecular hydrogen bonding due to:

a. Inter molecular hydrogen bonding between phenolic OH and nitrogen of aniline.
b. Carbonyl oxygen and amino hydrogen of aniline.
c. 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-1 – 1498cm-1). All the above spectral data confirm the formation of the title mixture due to intermolecular hydrogen bonding.



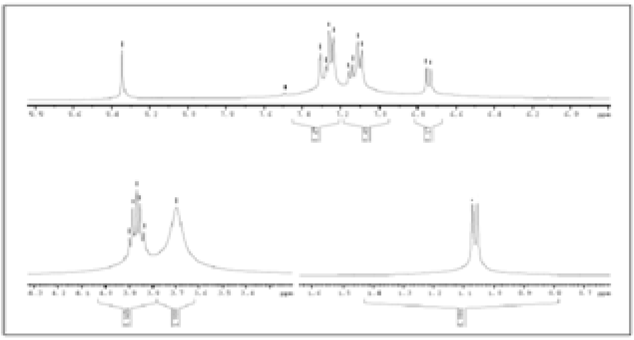


Figure 1: ^{1}H - NMR spectrum of 5- bromo salicylaldehyde with aniline in CCl_4 system

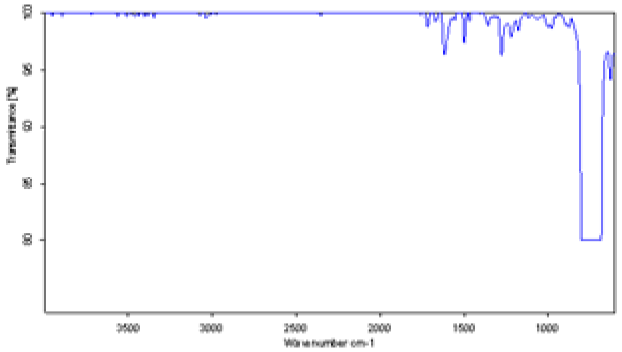


Figure 2: FTIR Spectrum of 5 –bromo salicylaldehyde with aniline in CCl_4 system

3.2 Density Measurement

The density was measured by a 10 ml specific gravity bottle calibrated with double distilled water and acetone. From the Table 1 it is seen that the density values are often higher compared to the parent aldehydes. It shows that the existence of strong intermolecular attractions and the formation of hydrogen bonding will reflect the higher density.

3.3 Viscosity measurement

An Ostwald's viscometer was used for viscosity measurements. Increasing the concentration of the solutions gives rise to an increase in viscosity. In the present study a dip at 0.04 mole fraction of 5–bromo salicylaldehyde and 0.018 mole fraction of aniline of the title mixture, the viscosity variation indicate that at this mole fraction, structure formation may be in equilibrium whereas at other mole fractions, the predominantly existing molecule may affect the other [9].

3.4 Refractive index measurement

Refractive indices were measured with an Abbe's refractometer (Erma A-302A) and the values were obtained for Na-D light with an error less than ± 0.0002 units. A halogen substituent like bromo is electron releasing by resonance but electron withdrawing because of its high electro negativity (Inductive effect). So the refractive index of the title mixture increases with its density [10].

3.5. Molecular acoustics and physico chemical behavioral studies

The above studies reveal that valuable information regarding the complex formation can be obtained through molecular acoustics investigation of two interacting solutes in an inert solvent. The ultrasonic velocity was measured using a single crystal ultrasonic Interferometer with an operating frequency of 2 MHZ supplied by M/S Mittal enterprises, New Delhi.

In the present system the ultrasonic velocity increases with increasing concentration of substituted bromo salicylaldehyde. The variation of ultrasonic velocity (υ) in a solution depends upon the increase or decrease of intermolecular free length (Lf) after mixing the compounds. Based on the model for sound propagation proposed by Eyring and kincaird [11], ultrasonic velocity (υ) should increase, if the intermolecular free length (Lf) decreases and vice versa. This fact was noticed in the present study of the system. In fact the molecular association increases ultrasonic velocity (υ), Acoustic impedance (Z), and cohesive energy (Ce) decreases intermolecular free length (Lf) and adiabatic compressibility (β).

A reduction in adiabatic compressibility (β) is an indication that component molecular are held close to each other. The decrease in the value of adiabatic compressibility (β) and intermolecular free length (Lf) with increase in utra sonic velocity (υ) further strengthens the strong molecular association between the unlike molecules through hydrogen bonding due to which structured arrangement is affected. Similar results were obtained by earlier workers [12].

From the Table 2 it is seen that the values of viscous relaxation time (τ), free volume (Vf) and internal pressure (πi) non-linear with the concentration of the title mixture. It happens due to the close packing of molecules inside the shield. The increase in internal pressure indicates also citation through hydrogen bonding and hence it supports the present investigation [13].

Table 1: Mole fractions of 5 bromo salicylaldehyde(X_1) , mole fractions of aniline(X_2) and Values of Ultra sonic Velocity (U), Density (ρ) Viscosity (η)and Refractive Index (D) of 5 - bromo salicylaldchyde + aniline + CCl_4

X_1	X_2	Ums^{-1}	ρkgm^{-3}	$\eta \times 10^3$ Nsm^2	D
0.01	0.004	908	1.6097	0.0008950	1.4898
0.02	0.009	911.5	1.6180	0.0009547	1.4899
0.03	0.013	935.5	1.6195	0.0009831	1.4980
0.04	0.018	998.5	1.6220	0.0009483	1.4992
0.05	0.023	935	1.7190	0.0009758	1.4927

Table 2: Mole fraction of 5-bromo salicyladehyde (X_1), Mole fraction of aniline (X_2),and values of Adiabatic Compressibility (β) Cohesive Energy (Ce) Free Length (L_f), Relaxation Time (τ), Internal pressure (πi) Adiabatic impedance (Z), Free Volume (V_f) of 5- bromo salicylaldehyde + Aniline + CCl_4

X_1	X_2	$\beta x\ 10^{-10}$ $(M^2\ N^{-1})$	$(Ce\ x\ 10^6)$ $kjmol^{-1}$	L_f x 10^{-10m}	τ x $10^{-12}S$	$\pi_i x10^6$ (NM^{-2})	$Zx10^6$ $kgm2S^{-1}$	V_f x 10^{-7} $m^3mol\text{-}1$
0.01	0.004	7.53500	7415.15	16.4150	0.8995	3.8676	1.46097	0.6256
0.02	0.009	7.4388	7619.58	16.3378	0.9469	3.9858	1.4748	0.5739
0.03	0.013	7.0577	7632.96	16.12197	0.9251	3.98031	1.5145	0.5737
0.04	0.018	6.1837	7247.73	15.5906	0.78187	3.77503	1.61956	0.67099
0.05	0.023	6.6542	7447.83	15.65019	0.8657	4.09878	1.60726	0.69996

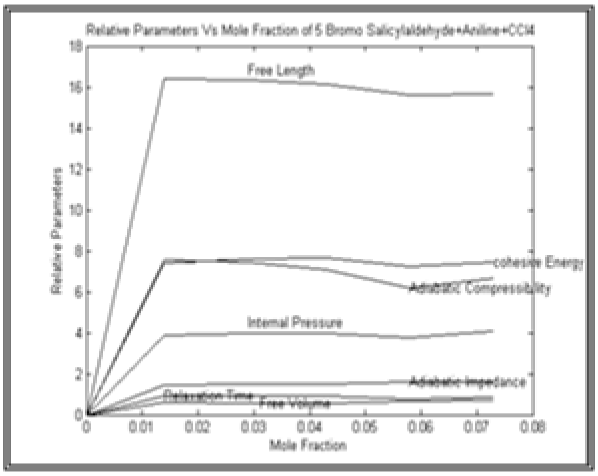


Figure 3: Graph between Free Length, Cohesive Energy, Adiabatic Compressibility, Internal Pressure, Adiabatic Impedance, Relaxation Time and Free Volume Vs Mole Fraction of 5 bromo salicylaldehyde + aniline+ CCl_4

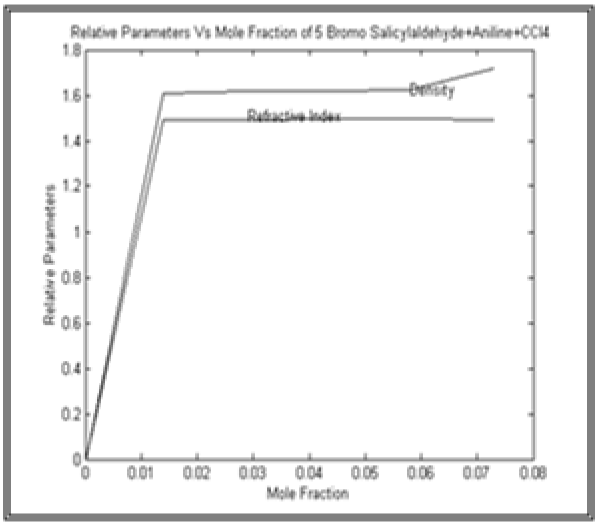


Figure 4: Graph between Density and Refractive Index Vs Mole Fraction of 5 bromo salicylaldehyde + aniline+ CCl_4

4. Conclusion

Hydrogen bonding to a carbonyl group causes a shift to lower frequency with electron withdrawing substituent such as bromo in the 5th position. The carbonyl absorption also disentangles fully the various effects such as inductive and mesomeric effects, bond angle changes and steric influences. Br, the ortho – para directing substituent, possesses the non bonding electron pair on the key atom.

From ^{1}H-NMR analysis the aromatic rings with a highly electronegative substituent such as bromine exhibit complex spectrum and also exert long large shielding effects on neighboring protons due to the steric disposition of the two interacting systems. The equilibrium present and the kinetic behavior of the title mixture have been investigated by the molecular acoustics techniques. The measurement of physical properties like density, viscosity and refractive index showed the strong intermolecular attractions between the title mixtures.

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