

frequency band of 5-FS and aniline mixture observed at 1733 cm^{-1} may be ascribed to the 1:1 complexes formed between the proton acceptor and the proton donor, due to the presence of intermolecular hydrogen bonding (see Banwell C.N⁸ in 1972). The bands at 1580, 1456, 1385, 1320 cm^{-1} were assigned to γ (N-H) bending, γ (O-H) bending and γ s (C-N) vibrations of the new compound . The two bands at 1353, 1170 cm^{-1} are due to the strong vibrations of aniline. The bands at 1251, 1202, 1140 , 1030 cm^{-1} are the in plane bending C-H vibrations of the new compound. The bands at 962, 908, 872, 783, 691, 673 cm^{-1} were assigned to out of plane bending vibrations of the C-H bands. The peak assignments have been made in consultation with literature values.

Table 1: Observed IR Frequencies (cm^{-1}) and band assignments for 5FS-A at room temperature

Frequencies	Assignments Observed IR frequencies
3364	N-H Stretching vibration (intermolecular)
2925,2851	C-H Stretching vibration of aldehyde group
2046,1943,1845,1621	Overtone combination regions of substitution of the ring
1871	Shift due to Fluorine stretching frequency
1733	C=O stretching due to intermolecular hydrogen bonding
1580	N-H bending
1456,1385	O-H bending
1353,1170	Aniline stretching frequency
1320	C-N stretching
1251, 1202,1140,1030	C-H in plane bending
962, 908,872,783,691,673	C-H out of plane bending

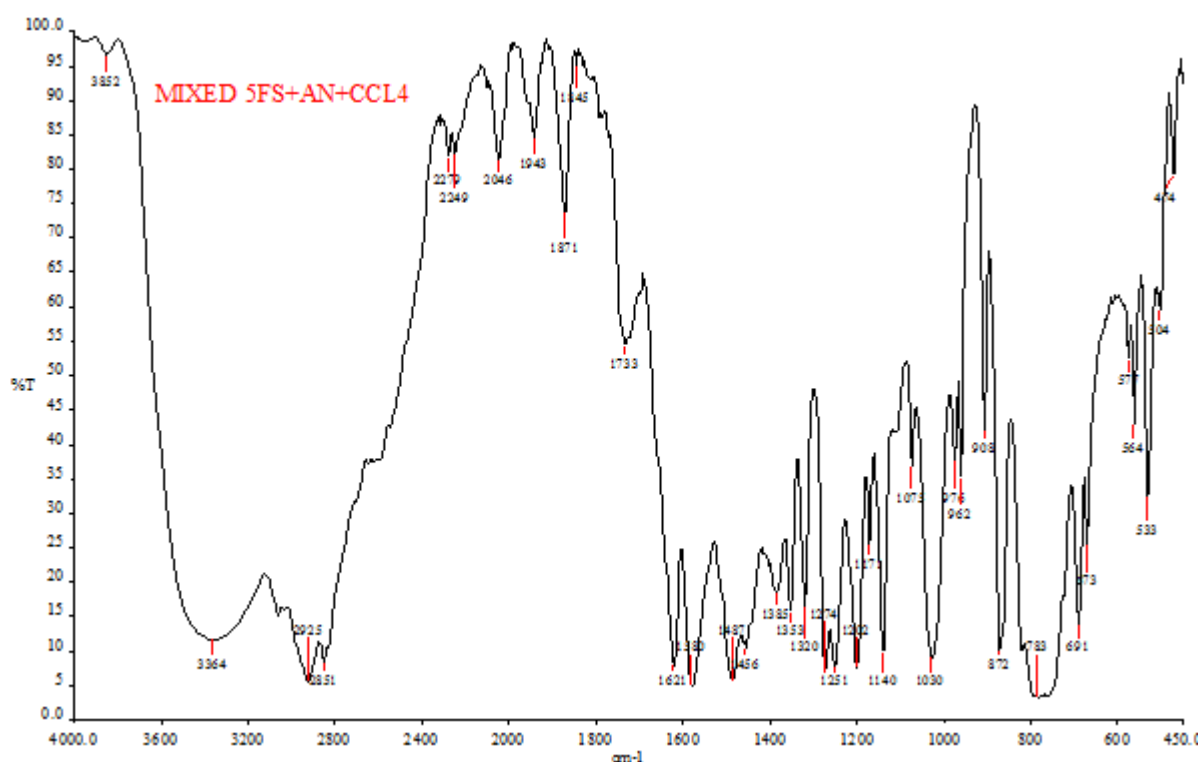


Figure 1: FT-IR Spectrum of 5-Fluoro salicylaldehyde- Aniline composite material

The ¹H-NMR spectra of the title composite material were recorded in CDCl₃. Aromatic rings with a highly electronegative substituent, such as Fluorine exhibit complex second order spectra. The figure shows the spectrum of the new material which might be referred to as system containing five interacting nuclei ABB'MM' system, where two protons α to fluorine are M and M' the three most distant protons are A BB'. Singlet at 8.594 ppm was assigned to aldehydic proton H₂ and multiplets at 7.479 ppm, 7.334 ppm, 7.135ppm, 7.020ppm were assigned to protons H₈, H_{3,4} H₅ and H₃ of mono-substituted benzene ring.

Multiplets at 1.578 ppm and 1.277 ppm were assigned to H₆ and H₄ protons of the fluorine. Multiplet at 4.0 ppm and 4.50 ppm were assigned to protons H₉, H₇ of amino exchangeable with 5-FS. Similar peak at 13.040 ppm has been reported due to long deshielding and the formation of the intermolecular hydrogen bonding of the new compound 5-FS-A. The signals observed in the NMR spectra are in good agreement with reported values in the literature (see Jag Mohan⁹ in 2003).

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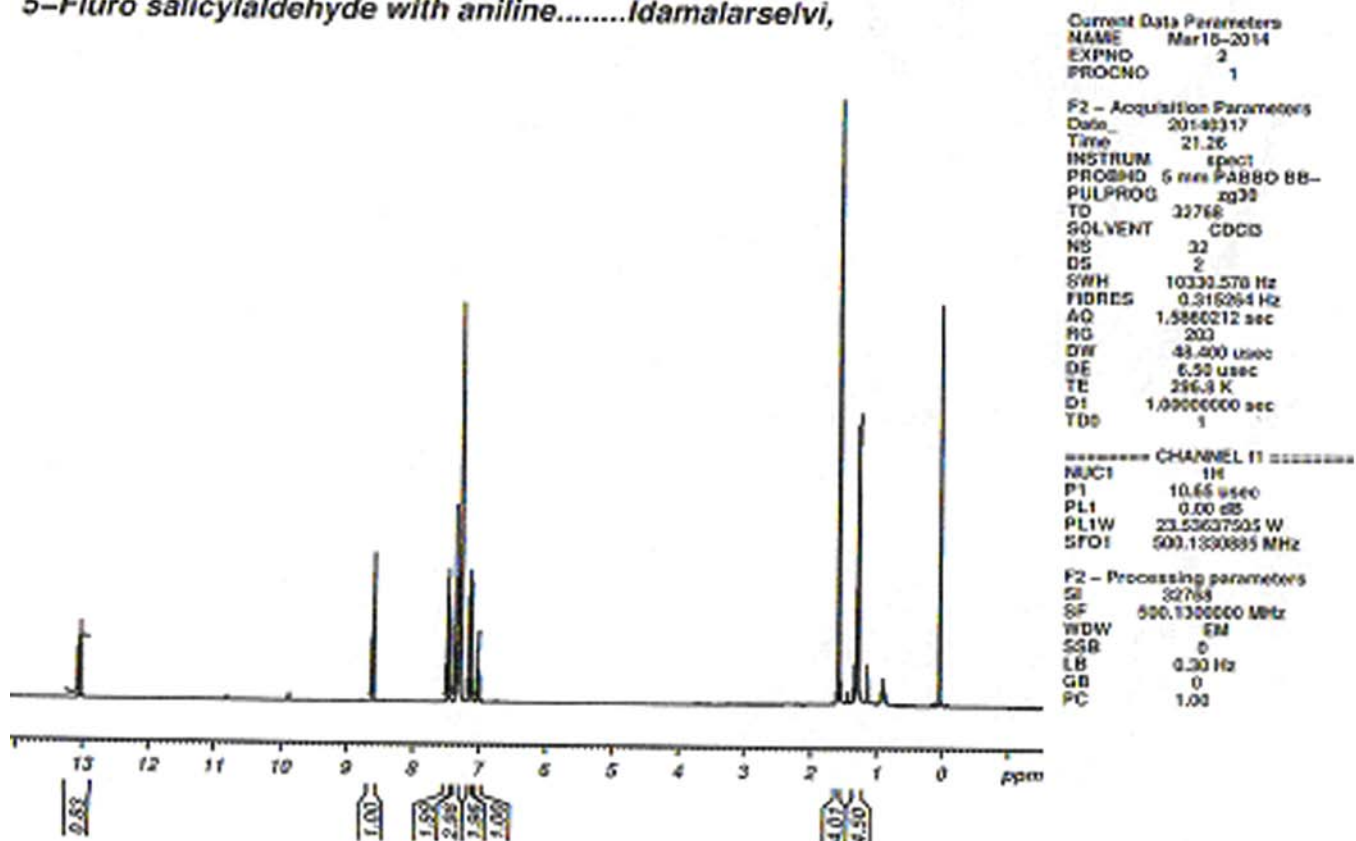


Figure 2: ¹H-NMR Spectrum of 5-Fluro salicylaldehyde- Aniline composite material

Ultrasonic studies has been increasingly used in organic synthesis in the last three decades .It has been demonstrated as an alternative energy source for organic reactions ordinarily accomplished by heating. Ultrasonic velocities of liquid mixtures containing polar and non- polar groups were of considerable importance in the formation of new compounds through intermolecular interaction between component molecules. There were higher variations in some intermediate concentration range given by Namato's¹⁰ relation (0.02m/l to 0.04 m/l 5FS+ 0.0132, 0.0199, 0.265m/l aniline in 5ml CCl₄) suggesting the existence of strong tendency of association between component molecules as a result of hydrogen bonding .The molecular association between the title mixtures have been investigated by measuring sound speed, viscosity, refractive index, densities and thermo acoustical parameters at 303k with different mole fractions in CCl₄ solutions were evaluated.

The variation of sound speed in a solution depends upon the increase or decrease of intermolecular free length (L_f) after mixing the compounds. Based on the sound propagation proposed by Eyring and Kincaid¹¹, sound speed should increase, if the intermolecular free length decreases and vice-versa. This fact noticed in the present system. A reduction in abiabatic compressibility is an indication that component molecules are held close to each other. The internal pressure of the new material in the present study increases with the increasing concentration of 5-FS can be attributed as there is definite interaction presents between the unlike components of the mixture. Similar results were reported by Rama Chandra Raja C et. al¹² in 2013 and R.A.Patil et. al¹³ in 2013. The experimental values and the thermo-acoustic parameters were listed in Table 2&3.

Table 2: Mole fractions of 5-FS (X₁), mole fractions of Aniline (X₂), Values of Density (ρ), viscosity (η), velocity(c) and Refractive index (D)

X ₁	X ₂	C ms ⁻¹	ρ kgm ⁻³	η x 10 ³ Nsm ²	D
0.04	0.0265	1476	1.5929	0.001493	1.4774
0.08	0.0531	1227	1.5970	0.007110	1.4778
0.12	0.0797	1117	1.6180	0.02022	1.4796
0.16	0.1063	812	1.6250	0.02215	1.4830
0.20	0.1329	734	1.6410	0.02461	1.4821

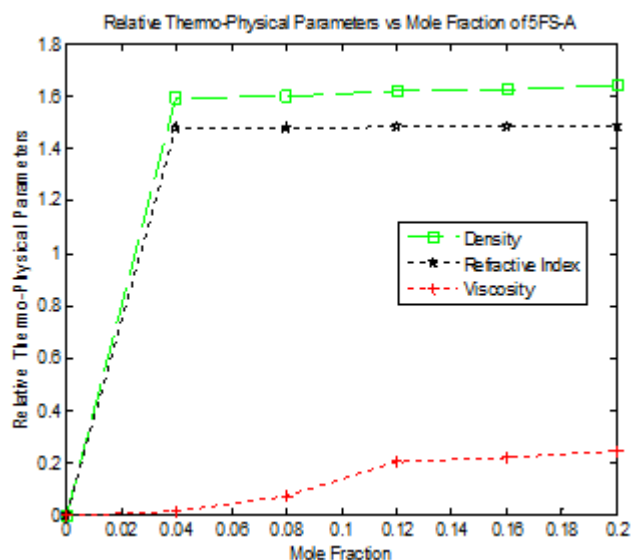


Figure 3: The MATLAB output of Thermo- Physical parameters vs Mole fractions of 5FS –Aniline mixture

The viscosity increases as the molar concentration of the solute mixture increases upto 100 mole % and mixture

further increase of the mole fraction of the solute mixture it still increases, it shows the strong formation of the new material. The similar results were reported by V.K.Syal et al¹⁴ in 2003. The density, viscosity and refractive index shows a increasing tendency due to the strong formation of the hydrogen bonding and the molecular association of the new material. The applicability of the more common mixing rules were studied. Same study was made by G.P Duebey et al¹⁵ in 2005. Rao's constant was found to be an additive relation that it can be calculated as a sum of increments from the atoms /atom groups in the molecule and from the chemical bonds under consideration. From the present study it is observed that Rao's constant varies non- linearly with the concentration. Estimation of salivation of organic liquid mixtures have been made by salivation number. Using Passynsky equation (Passynsky, 1943) the solvent molecules participating in the salivation were effectively incompressible due to strong localized electric fields. In the present study the salivation number has decreases with increase of concentration indicates that the number of solvated molecules "S" per monomer unit is high for lower concentration. As the concentration increases the number of monomer units increases and hence the value of "S" decreases.

Table 3: Mole fraction of 5FS (X_1), mole fraction of aniline (X_2), Values of adiabatic compressibility (β), internal pressure (π), free length (L_f), Rao's constant(R), Salivation number (S) of 5FS with aniline in CCl_4 .

X_1	X_2	$\beta \times 10^3$ ($N^{-1} m^2$)	$L_f \times 10^{-10} m$	$\pi \times 10^6$ (Mm^{-2})	R	$S \times 10^{-10}$
0.04	0.0265	6.9753	46.350	2.4375	4327.58	5.9501
0.08	0.0531	6.9574	47.036	2.7220	3588.28	2.9181
0.12	0.0797	6.8671	47.459	2.9241	3224.17	1.7568
0.16	0.1063	6.8376	48.073	3.4763	2333.67	1.2712
0.20	0.1329	6.7709	48.591	3.7334	2088.97	0.9337

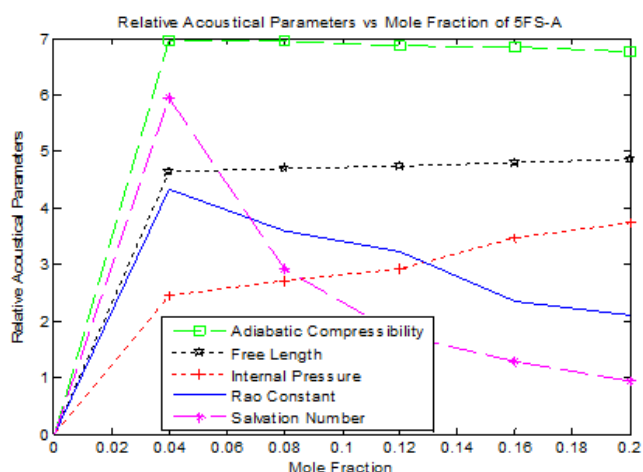


Figure 4: The MATLAB output of Acoustical Parameters vs Mole

Fractions of 5FS – Aniline mixture

4. Conclusions

The potential of weak second sphere interactions (C-H---F and C-H---O) in the binding of 5-Fluoro salicylaldehyde–aniline has been explored by forming and characterizing the

new composite material. As laid down as an objective at the outset to evaluate C-H---F interactions amid the presence of NH_2 group has shown that C-H---F interactions can indeed manifest in the new complex. Thus, it is important to consider the cooperative interplay of weak second sphere interaction of the kind C-H---F even in molecular system in which molecules are endowed with halogen substitution. Such consideration may facilitate the composite material of this kind of molecular system in which weak second sphere co-ordination has a marked influence even in the presence of strong O-H---N and N-H---O interactions.

The scope and generality of Ultrasonic process is illustrated with respect to various aromatic aldehydes. Aromatic aldehydes substituted with either electron- donating or electron – withdrawing groups have undergone smooth reaction and gave the corresponding reaction 5- Fluoro salicylaldehyde – Aniline in moderate to excellent yields. In general, it was found that the compounds having fluoro substitution along with salicylaldehyde and aniline systems exhibited good formation of composite material through hydrogen bonding.

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