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SYNTHESIS, CHARACTERIZATION AND ACOUSTICAL STUDY OF FLUORO METHYL CHALCONE

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ABSTRACT:

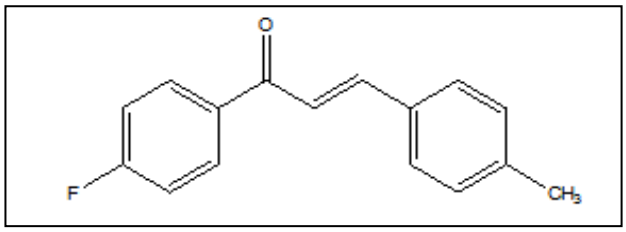
The density, viscosity and ultrasonic velocity have been measured for synthesized fluoro methyl chalcone in DMF and THF solutions of various concentrations at 300.15K with a view to understand the molecular interactions in these solutions. The experimental data have been used to calculate various acoustical parameters, which are interpreted in terms of solute-solute and solute-solvent interactions in different solvents.

Keywords: Fluoro methyl chalcone, density, viscosity, ultrasonic velocity, DMF, THF, acoustical parameters.

INTRODUCTION:

Chalcones are known as benzalacetophenones or benzylidene acetophenone.

Kostanecki and Tambor[1] gave the name Chalcone. The chemistry of chalcones has generated intensive scientific studies throughout the world, due to their biological and industrial



applications. Chalcones are characterized by their possession of a structure in which two aromatic rings are linked by an aliphatic three carbon chain. Different methods are available in the literature for the synthesis of chalcones[2-10]. The most convenient method is the one, which involves the Claisen-Schimidt condensation of equimolar quantities of aryl methyl ketones with arylaldehyde in presence of alcoholic alkali. The chalcones have been found to be useful for the synthesis of variety of heterocyclic compounds and are associated with different biological activities.

Now a days, lots of interest has been generated on the use of ultrasound radiation in synthetic organic chemistry, which includes decrease of reaction time, increase of yield, lower reaction temperature etc[11-14]. By ultrasonic sound velocity measurements, the molecular interactions in pure liquid [15-17], aqueous solutions [18-19] and liquid mixtures [20] have also been studied.

Several physico-chemical parameters are available in the list and few of them are of much interest. It was well understood by the literature that physico-chemical properties such as acoustical properties, density, viscosity, ultrasonic sound velocity, refractive index, etc. have contributed advancement in the physical sciences and also in daily human life. These properties are the sensitive indicators for understanding molecular interactions.

The study of physico-chemical properties of compounds in solutions gives complete understanding of the behavior of compounds in different solvents. Literature survey shows that very little work has been reported for the study of physico- chemical studies such as acoustical properties, density, viscosity, ultrasonic sound velocity, refractive index of the organic as well as heterocyclic compounds. Thus, in the present work, fluoro methyl chalcone was synthesized and characterized by IR and NMR spectra. Various physico-chemical properties and acoustical properties such as density, viscosity and ultrasonic sound velocity have been studied in dimethylformamide (DMF) and tetrahydrofuran (THF) for different concentrations of fluoro methyl chalcone solution were done at 308.15 K with a view to understand the molecular interactions in these solutions. From these experimental data, various acoustical parameters such as

isentropic compressibility, Rao's molar sound function, specific acoustical impedance, internal pressure, Vander Waals constant, free volume etc. were evaluated and results are discussed.

MATERIALS AND METHODS:

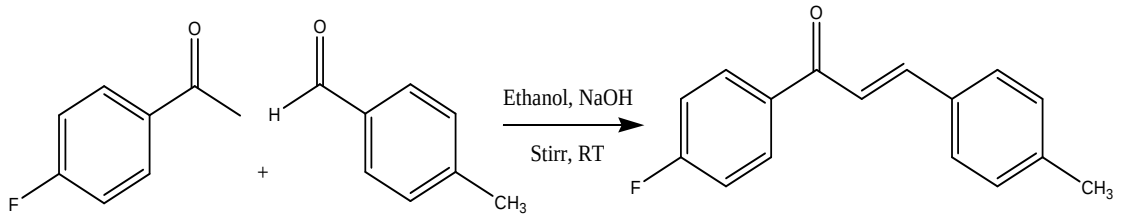
Experimental:

The title compounds was synthesized by Claisen-Schmidt condensation using ethanol as reaction medium. Melting points (^{o}C) were determined with a MELTEMP II capillary apparatus (LAB Devices, Holliston, MA, USA) without correction. IR spectra were recorded on FT-IR spectrometer (Perkin Elmer) using KBr disc method. ^{1}H NMR spectra were recorded on Brucker 400 MHz spectrometer in $CDCl_3$ as a solvent. TLC was performed on silica gel coated plates for monitoring the reactions.

The general procedure for the synthesis of fluoro methyl chalcone (FMC)

A mixture of 4-methyl benzaldehyde (1 mM) and 4-fluoroacetophenone (1 mM) was dissolved in 15 mL ethanol. To this mixture, sodium hydroxide (20%, 1mL) was added and the reaction mixture was stirred at room temperature for 12 h. After completion of the reaction (monitored by TLC), the crude mixture was worked up in ice-cold water (100 mL). The product which separated out was filtered and recrystallized from ethanol to afford title compound.

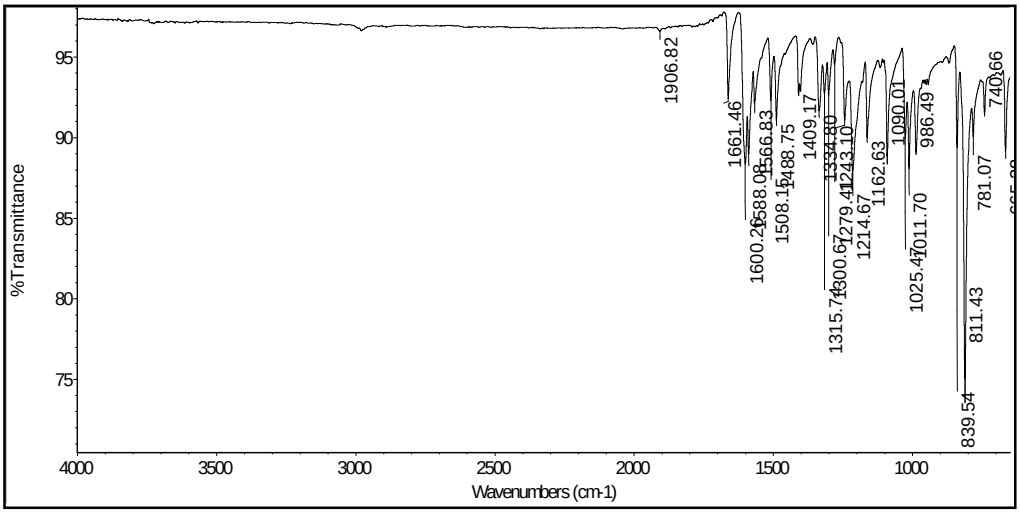
Scheme 1: Synthesis of Fluoro methyl chalcone (FMC)



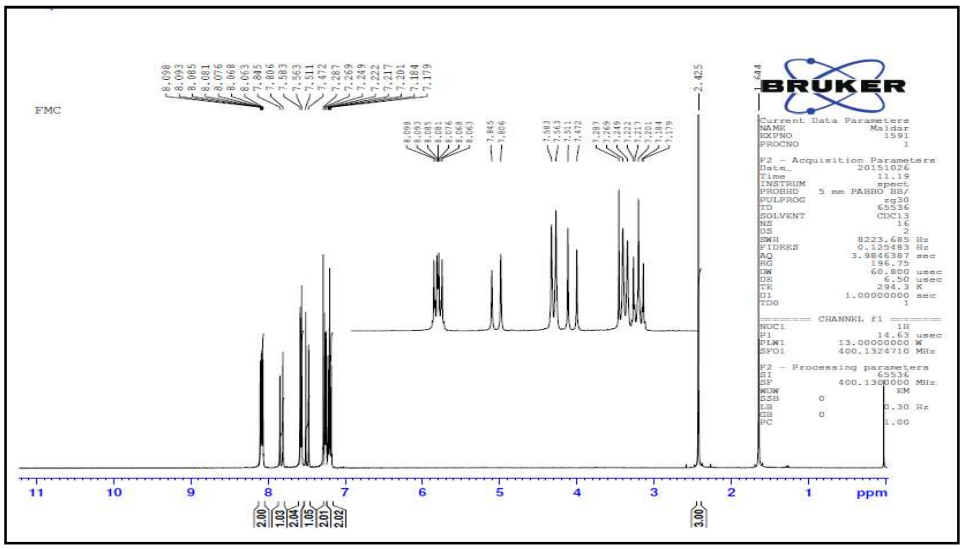
1-(4-Fluoro-phenyl)-3-p-tolyl-propenone

Molecular formula: $C_{16}H_{13}FO$, **yield** 92%; **m.p**. 165 ^{0}C; **IR** (cm^{-1}): 1661 (C=O group stretching), 1600 cm^{-1} (C=C bond) and 1588 (C=C stretching in aromatic ring); **^{1}H NMR** ($CDCl_3$): δ 2.425 (s, 3H, H-Methyl), 7.845-7.806 (d, 1H, 15.6 Hz, -CH=CH-), 7.511-7.472 (d, 1H, 15.6 Hz, -CH=CH-), 7.179-8.098 (m, 8H, ArH).

IR spectra of FMC compound



^{1}H NMR spectra of FMC compound



Choice of Solvents:

N,N-Dimethylformamide (DMF) and tetrahydrofuran (THF) have been chosen as solvents in the present work. The densities, viscosities and ultrasonic velocities of solvents and solutions of different concentration were measured at 300.15K by using pyknometer, an Ubbelohde suspended level viscometer and ultrasonic interferometer.

Density measurements:

The weight of distilled water, pure DMF and THF solvents and solutions of fluoro methyl chalcone (FMC in DMF and THF) was measured by using pyknometer. The densities were evaluated by using following equation:

$$\boldsymbol{\rho = \frac{(\text{wt.of solvent or solution})(\text{density of water})}{(\text{wt.of water})}\ g/cm^3}$$

Viscosity Measurements:

The viscosity of distilled water, pure DMF and THF solvents and solutions of FMC (in DMF and THF) were determined by using Ubbelohde viscometer [21]. The measured quantity of the distilled water / solvent / solution was placed in the viscometer, which was suspended in a thermostat at 300.15 K. The digital stopwatch, with an accuracy of + 0.01 sec was used to determine flow time of solutions. Using the flow times (t) and known viscosity of standard water sample, the viscosity of solvent and solutions were determined by using the following equation:

$$\frac{\eta_1}{\eta_2} = \frac{t_1\rho_1}{t_2\rho_2}$$

Ultrasonic velocity measurement:

Ultrasonic interferometer (Model No. F-81), Mittal Enterprise, New Delhi, working at frequency (F) of 2 MHz was used to determine sound velocity. The solvent / solution were filled in the measuring cell with quartz crystal and then micrometer was fixed. The circulation of water from the thermostat at 308.15 K was started and test solvent / solution in the cell is allowed to thermally equilibrate. The micrometer was rotated very slowly so as to obtain a maximum or minimum of anode current (n). A number of maximum reading of anode current were counted. The total distance (d) travel by the micrometer for n=10, was read. The wave length (λ) was determined according to the equation

$$\boldsymbol{\lambda = \frac{2d}{n}}$$

The sound velocity (U) of solvent and solutions were calculated from the wavelength and frequency (F) according to equation

$$U = \lambda F$$

RESULTS AND DISCUSSION:

From the experimental data of density(P), viscosity(η) and ultrasonic sound velocity(U) of pure solvents (DMF and THF) and the solutions of synthesized compound, various acoustical parameters like specific acoustical impendence (**Z**), isentropic compressibility (**κs**), intermolecular free length (**Lf**), molar compressibility (**W**), Rao's molar sound function (**Rm**), relaxation strength (**r**), relative association (**RA**), internal pressure (**π**), free Volume($\mathbf{V_f}$) etc. were calculated at 308.15 K using the following equations:

1. Specific acoustical impedance:

Specific acoustical impedance (Z) can be calculated as,

$$\mathbf{Z = U\rho}$$

2. Isentropic compressibility:

Isentropic compressibility (κs) can be evaluated according to the following the equation[22]

$$\mathbf{Ks} = \frac{\mathbf{1}}{\mathbf{U^2\rho}}$$

3. Intermolecular free path length:

Jacobson [23] proposed an equation to calculate the intermolecular free path length (Lf), which is given below:

$$\mathbf{L_f = K_j \kappa_s^{1/2}}$$

Where, K_j is Jacobson constant (=2.0965 X 10^{-6})

4. Molar compressibility:

Molar compressibility (W) can be calculated by the following equation [24]:

$$\mathbf{W} = \left(\frac{\mathbf{M}}{\boldsymbol{\rho}}\right)\mathbf{K_s}^{\frac{-1}{7}}$$

The apparent molecular weight (M) of the solution can be calculated according to equation

$$\mathbf{M = M_1 W_1 + M_2 W_2}$$

Where, W_1 and W_2 are weight fractions of solvent and solute, respectively. M_1 and M_2 are the molecular weights of the solvent and compounds respectively.

5. Rao's molar sound function:

Rao's molar sound function (Rm) can be evaluated by an equation given by Bagchi et al.[25]:

$$\boldsymbol{Rm} = \left(\frac{\boldsymbol{M}}{\boldsymbol{\rho}}\right)\boldsymbol{U}^{\frac{1}{3}}$$

6. Relaxation Strength:

The relaxation strength (r) can be calculated as follows[26]:

$$\mathbf{r} = \mathbf{1} - \left[\frac{\mathbf{U}}{\mathbf{U_\infty}}\right]^{\mathbf{2}}$$

Where, U∞ = 1.6 x 10^5 cm/sec.

7. Relative Association (R_A):

$$\mathbf{R_A} = \frac{\boldsymbol{\rho}}{\boldsymbol{\rho_o}}\left[\frac{\mathbf{U_0}}{\mathbf{U}}\right]^{\frac{1}{3}}$$

Where, U, U_0 and ρ, ρ_0 are ultrasonic velocities and densities of solution and solvent respectively.

8. Internal Pressure (π):

Suryanarayana and Kuppuswamy [27] gave the following equation for evaluating internal pressure:

$$\boldsymbol{\pi} = \mathbf{bRT}\left[\frac{\mathbf{K_n}}{\mathbf{U}}\right]^{\frac{1}{3}}\frac{\boldsymbol{\rho}^{\frac{2}{3}}}{\mathbf{M}^{\frac{7}{6}}}$$

Where, b is the packing factor (= 2). K is a constant (=4.28 X 10^9). The internal pressure **(π)** depends on temperature, density, ultrasonic velocity and specific heat at constant pressure.

9. Free Volume (V_f):

Free volume [28] can be calculated according to equation (1.15):

$$V_f = \left[\frac{MU}{K_n}\right]^{\frac{3}{2}}$$

In the present work, density, viscosity and ultrasonic sound velocity have been studied in DMF and THF for different concentrations of FMC at 300.15 K. It is observed that ultrasonic velocity (U) increases with increase in concentration of the compound. **Table - 2** and **4** showed that **Lf** decreases continuously, which suggest that there is strong interaction between solvent and compound molecule.

This is also supported by the variations of isentropic compressibility (κs) with concentrations of the compound for both solvents. From the obtained data, it was observed that both isentropic compressibility (**κs**) and relaxation strength (**r**) are decreases with concentrations. The decrease of **κs** with increasing concentration might be due to aggregation of solvent molecules around solute molecules indicating thereby the presence of solute-solvent interactions.

The increase of acoustical impedance (**Z**) further confirms the solute-solvent interactions in these systems. The properties like Rao's molar sound function (**Rm**), molar compressibility (**W**) and are observed to increase linearly with concentrations. The linear variation of these acoustical properties indicates absence of complex formation.

The internal pressure (**π**) is the results of forces of attraction and repulsion between the molecules in solutions. The data reported in **Table – 2** and **4** showed that internal pressure decreases with concentration, which indicates the decrease in cohesive forces. Although decrease in compressibility (**κs**), intermolecular free length (**Lf**), relaxation strength (**r**) and increase of velocity (**U**), viscosity (**η**) suggest predominance of solute-solvent interactions, the decrease in internal pressure indicates the existence of solute-solute interactions.

The free volume (**Vf**) of solute molecule at particular temperature and pressure depends on the internal pressure of liquid, in which it was dissolved. The decrease in molecular association causes an increase in free volume (**Vf**). Thus, free volume is an inverse function of internal pressure. It is evident from **Table - 2** and **4** that **Vf** increases with concentration. Hence, increase in free volume causes internal pressure to decreases, which indicates the solute-solute interactions. This suggests that both solute-solute and solute-solvent interactions exist in these systems.

Table 1:
Experimental data of density (ρ), ultrasonic velocity (U) and viscosity (η) with various concentration of FMC in DMF at 300.15K.

Conc. (M)	(ρ) g.cm^{-3}	(U) 10^{-5} cm.s^{-1}	(η)10^3 poise
DMF	**0.9376**	**1401.3**	**0.6594**
0.002	0.9410	1409.8	0.6384
0.004	0.9423	1418.2	0.6543
0.006	0.9427	1428.3	0.6700
0.008	0.9433	1436.5	0.7000
0.010	0.9438	1448.1	0.7466

Table-2:
Variation of acoustical parameters with concentration of FMC in DMF at 300.15.

Conc. (M)	Ks 10^{-4}	**Lf** (^{o}A)	**r** 10^{-5}	**Z .10^{-5}** g.cm^{-2}	**Rm.10^{2}** cm$^{-8/3}$.s-$^{1/3}$	**W.10^{2}** cm^{1}.dyn^{-1}	**π**	**Vf** (cm^{3})10^{-7}	**RA**
DMF	**5.1417**	**0.04753**	**7.1315**	**1.3480**	**8.8016**	**2.3045**	**45823**	**1.2156**	**1.0000**
0.002	5.3469	0.04848	6.7638	1.3266	8.6996	2.2840	5627.6	1.1835	1.0016
0.004	5.2766	0.04816	6.8566	1.3363	8.7142	2.2894	5386.7	1.1961	1.0010
0.006	5.2000	0.04781	6.9689	1.3464	8.7414	2.2942	4985.6	1.2110	0.9991
0.008	5.1376	0.04752	7.0609	1.3550	8.7618	2.2967	4756.2	1.2234	0.9979
0.010	5.0528	0.04723	7.1914	1.3667	7.8297	2.2983	4571.6	1.2403	0.9957

Table-3:
Experimental data of density (ρ), ultrasonic velocity (U) and viscosity (η) with various concentration of FMC in THF at 300.15K.

Conc. (M)	(ρ) g.cm^{-3}	(U) 10^{-5} cm.s^{-1}	(η)10^{3} poise
THF	**0.8684**	**1217.6**	**0.8545**
0.002	0.8686	1226.3	0.8552
0.004	0.8688	1235.4	0.8561
0.006	0.8692	1237.6	0.8569
0.008	0.8694	1250.8	0.8595
0.010	0.8697	1261.2	0.8612

Table-4:
Variation of acoustical parameters with concentration of FMC in THF at 300.15K.

Conc. (M)	κS 10^{-4}	**Lf** (A_o)	**r** **10^{-5}**	**Z .10^{-5}** g.cm^{-2}	**Rm.10^{2}** cm$^{-8/3}$.s-$^{1/3}$	**W.10^{-3}** cm^{1}.dyn^{-1}	**π**	**Vf** (cm^{3})10^{-7}	**RA**
THF	**7.2697**	**0.05648**	**5.2134**	**1.0952**	**8.9133**	**2.3267**	**4621.5**	**0.9613**	**1.0000**
0.002	7.6555	0.05800	4.8743	1.0652	8.8755	2.3226	4644.5	0.9408	0.9979
0.004	7.5417	0.05757	4.9617	1.0733	8.9060	2.3241	4635.2	0.9529	0.9957
0.006	7.4781	0.05759	4.9540	1.0731	8.9186	2.3277	4626.8	0.9574	0.9955
0.008	7.3523	0.05684	5.1113	1.0874	8.9587	2.3387	4620.8	0.9745	0.9957
0.010	7.2467	0.05664	6.8825	1.0946	8.9909	2.3455	4603.9	0.9883	0.9899

Figure 1: The variation of ultrasonic velocity (U) with concentration of FMC in DMF and THF at 300.15K.

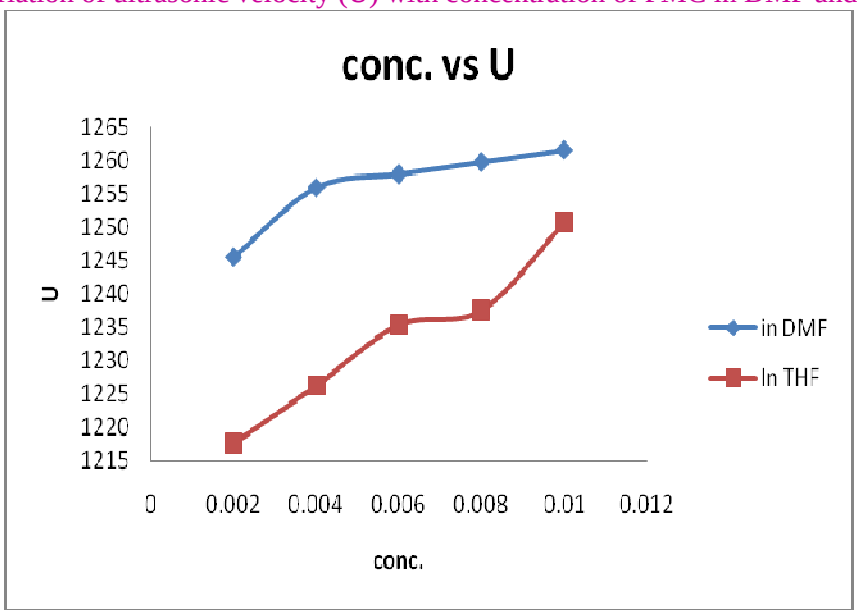
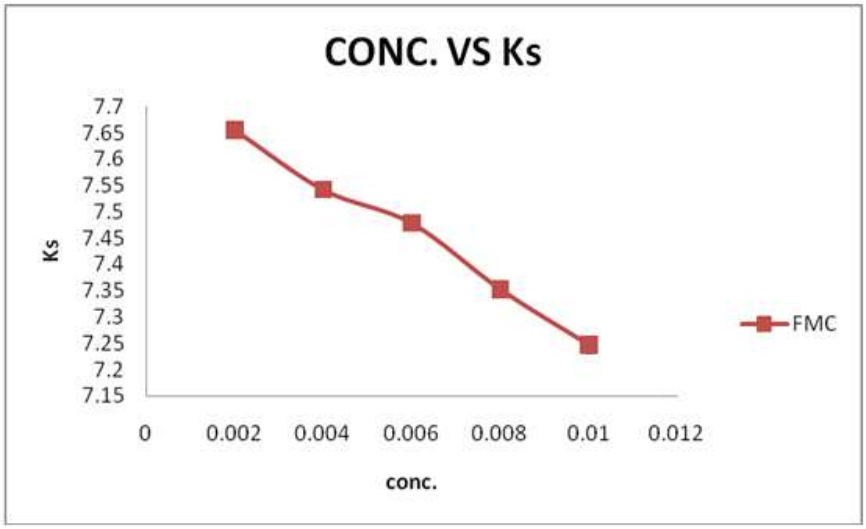


Figure 2: The variation of isentropic compressibility (κs) with concentration of FMC in DMF and THF at 300.15K



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