Synthesis and physical parameter study of Chloromethyl chalcone

Kallappa Mahajan[1], Shravan Jadhav[1] and Sitaram Chavan[1*]

[1]Department of Chemistry, DBF Dayanand College of Arts & Science, Solapur – 413002 (Maharashtra), India

Email: kjmahajan8275@gmail.com

ABSTRACT

The density, viscosity and ultrasonic velocity have been measured for synthesized chloro 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: Chloro methyl chalcone**,** density, viscosity, ultrasonic velocity, DMF, THF, acoustical parameters.

INTRODUCTION

Chalcones are known as benzalacetophenones or benzylidene acetophenone. Kostanecki and Tambor gave the name Chalcone (Cracknell, 1980). 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 (Hocheng *et al.*, 2002, Hromadkova *et al.*, 2002 and Vinatoru *et al.*, 1997). 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 (Jadhav *et al.*, 2013; Jadhav *et al.*, 2015). 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 (Krüger *et al.*, 1999). By ultrasonic sound velocity measurements, the molecular interactions in pure liquid (Bhatt *et al.*, 2000, Varma *et al.*, 2000), aqueous solutions and liquid mixtures (Kalidoss *et al.*, 2002) 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, chloro 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 chloro 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

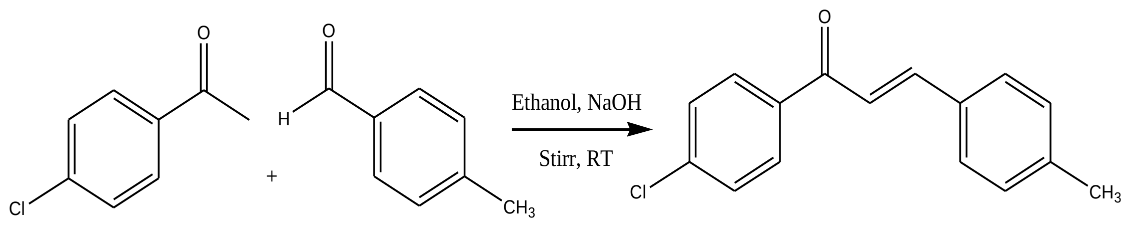
Experimental:

The title compounds were 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 Chloro methyl chalcone (FMC)

A mixture of 4-methyl benzaldehyde (1 mM) and 4-chloroacetophenone (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 Chloro methyl chalcone (CMC)



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

Molecular formula: $C_{16}H_{13}ClO$, **yield** 90%; **m.p**. 172 ^{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 2.42 (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-), 7.249-8.005 (m, 8H, ArH).

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.

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(V_f) etc. were calculated at 308.15 K using the standard equations (Mahajan et al., 2016).

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.

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

Conc. (M)	Density (ρ) g.cm^{-3}	Velocity (U) 10^{-5} cm.s^{-1}	Viscosity (η)10^{3} poise
DMF	**0.9376**	**1401.3**	**0.6594**
0.002	0.9352	1439.2	0.6942
0.004	0.9355	1442.2	0.7192
0.006	0.9358	1444.8	0.7362
0.008	0.9362	1446.o	0.7645
0.010	0.9364	1447.8	0.7691

Table 2: Variation of acoustical parameters with concentration of CMC in DMF at 300.15

Conc. (M)	Ks 10^{-4}	Lf (°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	5.1348	0.04751	7.1676	1.3468	8.8516	2.3119	4575.4	1.2212	0.9999
0.004	5.1376	0.04750	7.1541	1.3472	8.8853	2.3138	4563.3	1.2328	1.0001
0.006	5.1511	0.04743	7.1247	1.3461	8.6773	2.3159	4556.1	1.2334	0.9998
0.008	4.8400	0.04683	7.0910	1.4356	8.6783	2.3178	4549.4	1.2378	0.9991
0.010	4.6731	0.04668	7.3699	1.3454	7.7771	2.3190	4541.3	1.2421	0.9989

Table 3: Experimental data of density (ρ), ultrasonic velocity (U) and viscosity (η) with various concentration of CMC in THF at 308.15K

Conc. (M)	(ρ) $g.cm^{-3}$	(U) 10^{-5} $cm.s^{-1}$	$(\eta)10^{3}$ poise
THF	0.8684	1245.6	0.4179
0.002	0.8662	1256.0	0.4043
0.004	0.8673	1258.0	0.4080
0.006	0.8684	1259.8	0.4148
0.008	0.8695	1261.6	0.4247
0.010	0.8704	1262.1	0.4378

Table 4: Variation of acoustical parameters with concentration of CMC 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	7.2754	0.05646	5.2173	1.0928	8.9307	2.3336	4622.3	0.9753	0.9975
0.004	7.2646	0.05650	5.1996	1.0926	8.9644	2.3373	4617.8	0.9796	0.9969
0.006	7.2768	0.05647	5.1819	1.0924	8.9469	2.3430	4611.6	0.9838	0.9970
0.008	7.2732	0.05643	5.1622	1.0920	8.9504	2.3453	4606.2	0.9878	0.9975
0.010	7.2710	0.05634	5.0548	1.0841	8.9818	2.3478	4602.2	0.9903	0.9984

CONCLUSION

In summary, the title compound was synthesized conveniently and tested for various physical parameters. The result reveals 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.

REFERENCES

Bhatt S. C., Semwal H., Lingwal V., Singh K. and Semwal B. S. (2000). Acoustical parameters of some molecular liquids. *J. Acous. Soc.* India. 28: 293

Cracknell, A. P. (1980). "Ultrasonics", Chapter 6, 92, Wykenham Publishers.

Hocheng H. and Kuo K. L. (2002). Fundamental study of ultrasonic polishing of mold steel. *Int J Mach Tool Manu.* 42: 7.

Hromadkova Z., Ebringerova A. and Valachovic P. (2002). Ultrasound-assisted extraction of water soluble polysaccharides from the roots of valerian. *Ultrason Sonochem.* 9, 37.

Jadhav S. Y., Bhosale R. B., Shirame S.P., Patil S. B. and Kulkarni S. D. (2015). PEG Mediated Synthesis and Biological Evaluation of Asymmetrical Pyrazole Curcumin Analogues as Potential Analgesic, Anti-Inflammatory and Antioxidant Agents. *Chem Biol Drug Des.* 85, 377–384.

Jadhav, S.Y., Bhosale, R.B., Shirame, S.P., Sonawane, V.D., Hublikar, M.G., Sonawane, K.D. and Shaikh, R.U. (2013). Synthesis and biological evaluation of fluorohydroxy substituted pyrazole chalcones as anti-inflammatory, antioxidant and antibacterial agents. *Int. J. Pharm. Bio. Sci.* 4, 390–397.

Jadhav S.Y., Shirame S.P., Kulkarni S.D., Patil S.B., Pasale S.K. and Bhosale R.B. (2013). PEG mediated synthesis and pharmacological evaluation of some fluoro substituted pyrazoline derivatives as anti-inflammatory and analgesic agents. *Bioorg. Med. Chem. Lett.* 23, 2575-2578.

Kalidoss M. and Ravi S. (2002). Statistical Mechanics and its application, 312, 59.

Krüger O. and Peters D., (1999). Sonochemical treatment of natural ground water at different high frequencies: preliminary results. *Ultrason. Sonochem.* 6, 123.

Mahajan K. J., Jadhav S. Y. and Chavan S. K. (2016). Synthesis, characterization and acoustical study of fluoro methyl chalcone, *Golden Research Thoughts.* 6(6), 1-8.

Varma R. P. and Kumar S. (2000). Ultrasonic velocity and density measurements of ammonium soaps in 2-propanol. *Ind. J. Pure and Appl. Phy.* 38, 96.

Vinatoru M., Toma M., Radu O., Filip P. I., Lazurca D. and Mason T. J. (1997). The use of ultrasound for the extraction of bioactive principles from plant materials. *Ultrason. Sonochem.* 4, 135.