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ACOUSTICAL STUDY OF CHALCONES SYNTHESIZED BY GREEN PROTOCOL USING LiOH.H_2O CATALYZED ALDOL CONDENSATION

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Abstract

In the present investigation we have synthesized some substituted chalcones by environmental benign way using LiOH.H_2O as a green catalyst.The ultrasonic velocity (v), density (ρ) and viscosity (η) have been measured for the solutions of synthesized dibenzalacetone in ethanol as a solvent in different concentrations (0.1%,0.05%,0.025%,0.0125%). Ultrasonic parameters provide valuable information about various inter and intra molecular interactions in solution. Ultrasonic parameters such as adiabatic compressibility(β_{ad}),intermolecular free length(L_f) , relaxation time (τ)),free volume (V_f),internal pressure (Π_i),acoustic impedence(Z), surface tension(S), attenuation(a/f^2),Rao's constant(R),molar volume(Vm),cohesive energy(CE) of these solutions are computed on the basis of velocity, viscosity and density measurements. Various molecular interactions in these solutions have been analyzed on the basis of the variation of these parameters with concentration.

Keywords: Green synthesis ; ultrasonic velocity; adiabatic compressibility; acoustic impedance; relaxation time; ultrasonic attenuation; molecular interaction

Introduction

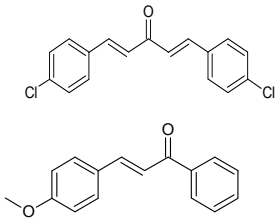
Aldol Condensation [1] is an extremely useful carbon-carbon bond-forming reaction in organic chemistry. Commercially available lithium hydroxide monohydrate (LiOH·H_2O) is found to be a novel 'dual activation' catalyst for tandem cross-aldol condensation between ketones and aromatic aldehydes leading to an efficient and easy synthesis of substituted chalcones at room temperature in short times. The reaction of aryl aldehydes with ketones afforded excellent yields .

The fact that the use of stronger bases such as NaOH, KOH and CsOH afforded inferior results suggested that $LiOH{\cdot}H_2O$ plays the dual role[2-4], i.e. generates the enolate from the ketone and activates the aldehyde carbonyl by coordination with Li+.

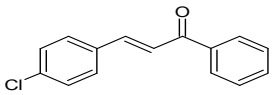
In the recent years, measurement of the ultrasonic velocity is helpful to interpret solute-solvent, ion-solvent interaction in aqueous and non aqueous medium [5-9]. The ion solvent interaction in aqueous $MnCl_2$ solution [10]can be calculated by interferometer .Furthermore it is an important tool for determination of adiabatic compressibility, internal free length and acoustic relaxation time of aqueous antibiotic cofotaxime sodium[11], some substituted pyrazolines in binary mixture acetone-water [12]. The ultrasonic studies on molecular interactions of substituted heterocyclic compounds in acetone water mixture at 303° K[13] have also been reported. Similarly it is useful for the determination of Ultrasonic parameters of lanthanide salt[14] , solution of cypermethrin with xylene and ethanol[15], PEG-8000[16], substituted heterocyclic compounds [17], citric acid in water at different temperature[18], non aqueous solution of metal complex [19], mixture of amines and amide in benzene [20], binary mixture of 1-propanol and water[21] .

Since, no work has been reported on the study of molecular interactions in ethanolic solution of synthesized chalcones , therefore in the present paper the determination of various acoustical parameters viz. adiabatic compressibility(β_{ad}),intermolecular free length(L_f) , relaxation time (τ)),free volume (V_f),internal pressure (Π_i),acoustic impedence (Z), surface tension(S), attenuation(a/f^2), Rao's constant(R),molar volume(Vm), cohesive energy(CE) of ethanolic solution of chalcones in different concentrations at 313 K have been carried out in order to understand the molecular structure of the compounds and the solute solvent

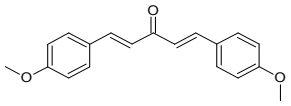
interaction in the solution.The compounds under investigation are as follows,



1a



2a



1b

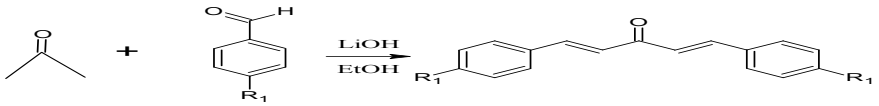
2b

Experimental

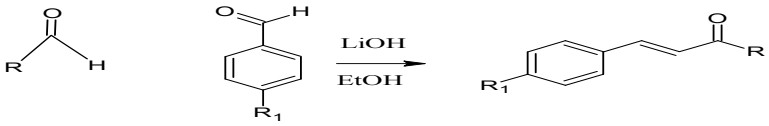
The chemicals used were of analytical grade. Double distilled water was used for preparation of solutions. Synthesized Chalcones (1a-1b&2a-2b) was dissolved in ethanol (99%) in various ratio to prepare different concentration 0.1%,0.05%,0.025%,0.0125%. The ultrasonic velocities of alcoholic solutions were measured using Multifrequency ultrasonic interferometer (model F-81) Mittal make operating at the frequency of 1 MH_Z with the accuracy of ±0.01 ms^{-1}. The densities (ρ) of solutions were determined using specific gravity bottles of capacity 10ml. The viscosities (η) of the solutions are measured using Oswald's viscometer. The temperature was kept 313 K during the measurement of ultrasonic velocity, density, and viscosity values.

General method of synthesis of chalcone

In a 25 mL round bottom flask containing a small magnetic bar, the aldehyde and ketone were taken with ethyl alcohol (5ml) and lithium hydroxide monohydrate (42 mg) monohydrate was added into it. The reaction mixture was magnetically stirred vigorously for 8-20 minutes. The solid precipitated out, 5 g of crushed ice was added and the solid was allowed to settle down. The precipitated solid was filtered, washed with water, air dried and recrystallized with ethanol.



Scheme:1:Synthesis of Chalcone (1a,1b,1c,1d) from acetone



Scheme:2: Synthesis of Chalcone (2a-2b)from substitutes acetones

Acoustical parameters

In the present investigation, solutions were prepared by adding the known weight of compounds. The study was done in different concentrations. With the help of measurements of ultrasonic velocity ,density and viscosity various acoustical parameters were calculated by using the following expressions.

1.Ultrasonic velocity (υ): The relation used to determine the ultrasonic velocity is given by,

$\upsilon = f\lambda \ ms^{-1}$

Where, f - Frequency of ultrasonic waves, λ - Wave length

2.Adiabatic compressibility (κ): Adiabatic compressibility which is defined as,

$\kappa = (1/\upsilon 2\ \rho)\ \ kg^{-1}\ ms^{2}$

Where, υ – Ultrasonic velocity, ρ – Density of the solution.

3. Free volume (V_f): Free volume in terms of the ultrasonic velocity (υ) and the viscosity of the liquid (η) as

$Vf = (M\ \upsilon/k\eta)^{3/2}\ m^3$

Where, M is the molecular weight and 'k' is a temperature independent constant equal to $4.28x10^9$ for all liquids.

4. Acoustic impedance (Z): The acoustic impedance is computed by the formula

$Z = \upsilon \times \rho \ kgm^{-2}s^{-1}$

5. Free length (L_f): Intermolecular free length is calculated by using the formula

$Lf = (K/\upsilon \rho^{1/2})\ m$

Where K - Jacobson temperature dependent constant defined as $K = (93.875 + 0.345T) \times 10^{-8}$

6. Absorption coefficient (α/f^2): It is calculated by

$\alpha/f^2 = 8\pi^2\eta/3\rho\upsilon^3$

7. Viscous relaxation time (τ): It is calculated using the relation,

$\tau = 4\eta/3\rho\upsilon^2$

8. Rao's Constant (R): Rao's constant can be calculated by using formula,

$R = V.v_3^1$ or $R = \left(\frac{M}{\rho}\right) v_3^1$

9. Surface Tension (S) : Surface tension can be calculated with the help of formula given below,

$v = (S/6.3 \times 10^{-4} \rho)^{2/3}$

10. Internal pressure (Π_i): Internal pressure can be calculated by formula given below,

$$\Pi i = b\ RT \left[\frac{k}{v}\right]^{1/2} \frac{\rho_3^2}{M_6^7}$$

11.Molar volume(V_m): It is the ratio of density verses molecular weight.

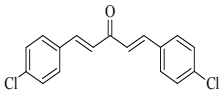
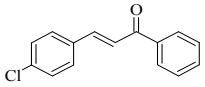
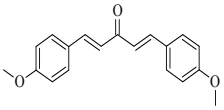
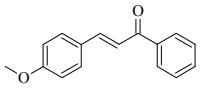
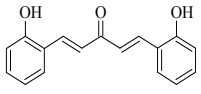
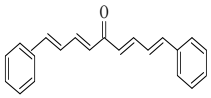
$$Vm = \frac{M}{\rho}$$

Results and Discussion

The measured values of ultrasonic velocity, density, viscosity and various calculated acoustical parameters were presented in figures 1 and 2. It is seen that the Density decreases with the concentration. Viscosity of the liquid increases with the increasing concentration suggesting more association between solute and solvent molecules. The ultrasonic velocity depends upon the intermolecular free length. The

velocity decreases with increase in concentration which suggests that the dipole - induced dipole interaction is larger than the induced dipole induced dipole interactions in which linear plots are obtained. The intermolecular free length increase due to greater force of interaction between solute and solvent by forming hydrogen bonding. Free volume decreases with the increase in concentration. The increase of adiabatic compressibility with concentration of solution may be due to collection of solvent molecule around ions, this supporting weak ion-solvent interaction. Internal pressure increases with the concentration of solution .The Rao's constant decreases and Relaxation time increases with concentration . Surface tension is inversely proportional to the concentration of solution . Cohesive energy , Molar volume, Ultrasonic attenuation increases (fig.2) with increasing concentration . It may be also be assumed that solvent-solvent interaction bring about a bonding between them.

Physical characterization of the synthesized compounds are given in the Table.1.

Sr. No.	*Compound*	*Time (min.)*	*Molecular formula*	*Molecular weight*	*% yield*	*Melting point*	*Structure*
1	1a	15	$C_{17}H_{12}Cl_2O$	303.18	18.38	220°C	
2	2a	18	$C_{15}H_{11}ClO$	242.70	22.48	212°C	
3	1b	15	$C_{19}H_{18}O_3$	294.34	30.01	223°C	
4	2b	20	$C_{16}H_{14}O_2$	238.28	35.81	230°C	
5	1c	15	$C_{17}H_{14}O_3$	266.29	23.12	260°C	
6	1d	20	$C_{22}H_{22}O$	302.40	23.77	266°C	

Spectroscopic data for the synthesized compounds are given below:

1,5-bis(4-chlorophenyl)penta-1,4-dien-3-one (1a):IR(Cm^{-1}): 2978(C-H);1713(C=O);1012(C-O);1600-1500(C=C of aromatic ring);870-675(C-H, phenyl ring substitution band)

3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (2a): IR(Cm^{-1}): 2918-2834(C-H); 1678(C=O);1091(C-O);1080(C- Cl in aromatic); 1600-1500(C=C of aromatic ring);870-675(C-H, phenyl ring substitution band)

1,5-bis(4-methoxyphenyl)penta-1,4-dien-3-one (1b): IR(Cm^{-1}): 3026(C-H); 1671(C=O);1091 (C-O); 1596(C=C of aromatic ring);870-675(C-H, phenyl ring substitution band) ^{1}HNMR;($CDCl_3$,300.13MHz); 1.88(4H,Ar); 1.00(2H); 1.12(2H); 1.88(dd,4H); 4.78(3H,s):^{13}C (75.47 MHz,$CDCl_3$); 40,129,130,140,167.4,190.80

3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one(2b) : IR(Cm^{-1}): 2935-2800(C-H); 1680(C=O);1110 (C-O); 1600-1500(C=C of aromatic ring);870-675(C-H,phenyl ring substitution band)

1-(2-hydroxyphenyl)ethanone(1c) : IR(Cm^{-1}): 3587(O-H); 2937-2800(C-H); 1678(C=O);1104 (C-O); 1600-1500(C=C of aromatic ring);870-675(C-H,phenyl ring substitution band)

1-phenyldeca-1,3,6,8-tetraen-5-one – benzene(1d) : IR(Cm^{-1}): 3027(C-H); 1671(C=O);1072 (C-O); 1573(C=C of aromatic ring);870-675(C-H,phenyl ring substitution band)

The measured values of velocity, Density, Viscosity, Adiabatic compressibility, Intermolecular free length, Free volume , Rao's constant and Internal pressure, Acoustic Impedence, Relaxation time, Ultrasonic attenuation, Surface tension, Cohessive energy of different concentration of solution of compounds are given in Table.2 and Table.3.

Table.2 -Ultrasonic velocity, Density, Viscosity, Adiabatic compressibility, Intermolecular free length, Free volume , Rao's constant of different % concentration of solution of compounds in ethanol at 313 K.

Solution of 1,5-bis (4-chlorophenyl) penta-1,4-dien-3-one (1a)

Concentration(%)	Density (Kgm^{-3})	Viscosity $x10^{3}$ (Nsm^{-2})	Ultrasonic Velocity (m/s)	Adiabatic compressibility $x10^{-11}$ (m^{2} /N)	Intermolecular free length $x10^{-11}$ (m)	Free Volume $x10^{-2}$ (m^{3} mol^{-1})	Rao's constant
0.0125	941	2.518	1200	0.737	5.483	3.472	3.523
0.025	930	2.924	1160	0.799	5.706	2.992	3.534
0.05	926	2.933	1090	0.908	6.085	2.708	3.467
0.1	916	2.914	1082	0.9325	6.1641	2.7053	3.4967

Solution of 3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (1b)

Concentration(%)	Density (Kgm^{-3})	Viscosity $x10^{3}$ (Nsm^{-2})	Ultrasonic Velocity (m/s)	Adiabatic compressibility $x10^{-10}$ (m^{2} /N)	Intermolecular free length $x10^{-11}$(m)	Free Volume $x10^{-2}$ (m^{3} mol^{-1})	Rao's constant
0.0125	951	2.559	1151	0.793	5.685	2.548	2.672
0.025	923	2.603	1123	0.859	5.916	2.443	2.731
0.05	919	2.778	975	1.144	6.829	1.987	2.616
0.1	900	2.978	970	1.180	6.367	1.963	2.666

Solution of 1,5-bis(4-methoxyphenyl)penta-1,4-dien-3-one(1c)

Concentration (%)	Density (Kgm -3)	Viscosity $x10^{3}$ (Nsm^{-2})	Ultrasonic Velocity (m/s)	Adiabatic compressibility $x10^{-10}$ (m^{2} /N)	Intermolecular free length $x10^{-11}$(m)	Free Volume $x10^{-2}$ (m^{3} mol^{-1})	Rao's constant
0.0125	845	2.603	1174	0.862	5.929	3.096	3.670
0.025	839	2.694	1130	0.933	6.167	3.033	3.649
0.05	834	2.774	1126	0.945	6.207	2.787	3.667
0.1	815	2.782	1087	1.038	6.504	2.683	3.709

Solution of 3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (1d)

Concentration(%)	Density(Kgm^{-3})	Viscosity x10^3 (Nsm^{-2})	Ultrasonic Velocity (m/s)	Adiabatic compressibility x10^{-10} (m^2 /N)	Intermolecular free length x10^{-11} (m)	Free Volume x10^{-2} (m^3 mol^{-1})	Rao's constant
0.0125	859	2.397	1118	0.9313	6.1604	2.591	2.875
0.025	849	2.517	1106	0.9629	6.263	2.442	2.899
0.05	841	2.615	1091	0.9989	6.380	2.319	2.913
0.1	835	2.717	1037	1.113	6.736	2.125	2.885

Table.3- Internal pressure, Acoustic Impedence, Relaxation time, Ultrasonic attenuation, Surface tension, Cohessive energy and Molar volume at 313 K.

Solution of 1,5-bis(4-chlorophenyl)penta-1,4-dien-3-one (1a)

Concentration(%)	Internal pressure (Nm^{-2})	Acoustic Impedence (Kg^{-1} m^2 S^{-1})	Relaxation time x10^{-12} (S)	Ultrasonic attenuation x10^{-14} (s^2m^{-1})	Surface tension(N/m)	Cohessive energy (KJ/Mole)	Molar volume (m^3/mol)
0.0125	58296	1129200	2.477	4.071	90.64	19328	0.3315
0.025	62311	1078800	3.009	5.116	87.05	20904	0.3354
0.05	65314	1009340	3.554	6.431	83.35	22006	0.3369
0.1	64878	991112	3.624	6.604	82.54	22098	0.3406

Solution of 3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (1b)

Concentration(%)	Internal pressure (Nm^{-2})	Acoustic Impedence (Kg^{-1} m^2 S^{-1})	Relaxation time x10^{-12} (S)	Ultrasonic attenuation x10^{-10} (s^2m^{-1})	Surface tension (N/m)	Cohessive energy (KJ/Mole)	Molar volume (m^3/mol)
0.0125	81278	109460	2.705	4.368	88.57	20725	0.2549
0.025	81165	103652	2.9820	5.236	84.90	21328	0.2627
0.05	89724	896025	1.0600	8.575	77.12	23678	0.2639
0.1	89041	873000	4.406	8.959	76.14	23987	0.2694

Solution of 1,5-bis(4-methoxyphenyl)penta-1,4-dien-3-one (1c)

Concentration(%)	Internal pressure (Nm^{-2})	Acoustic Impedence (Kg^{-1} m^2 S^{-1})	Relaxation time $x10^{-12}$ (S)	Ultrasonic attenuation $x10^{-10}$ (s^2m^{-1})	Surface tension (N/m)	Cohessive energy (KJ/Mole)	Molar volume (m^3/mol)
0.0125	59784	992030	2.994	5.006	84.09	20800	0.347
0.025	61696	948070	3.352	5.851	81.71	21619	0.3504
0.05	62472	939084	3.498	6.126	81.309	22022	0.3525
0.1	62698	885905	1.155	6.987	78.61	22617	0.3607

Solution of 3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (1d)

Concentration(%)	Internal pressure in (Nm^{-2})	Acoustic Impedence (Kg^{-1} m^2 S^{-1})	Relaxation time $x10^{-12}$ (S)	Ultrasonic attenuation $x10^{-10}$ (s^2m^{-1})	Surface tension (N/m)	Cohessive energy (KJ/Mole)	Molar volume (m^3/mol)
0.0125	76062	960362	2.977	5.252	81.99	21074	0.2270
0.025	77748	938994	2.232	5.762	80.98	21795	0.2803
0.05	79286	917531	3.483	6.296	79.91	22437	0.2829
0.1	82502	865895	1.210	7.673	77.00	23514	0.2850

The following figures shows the effect of concentration on various acoustical parameters.

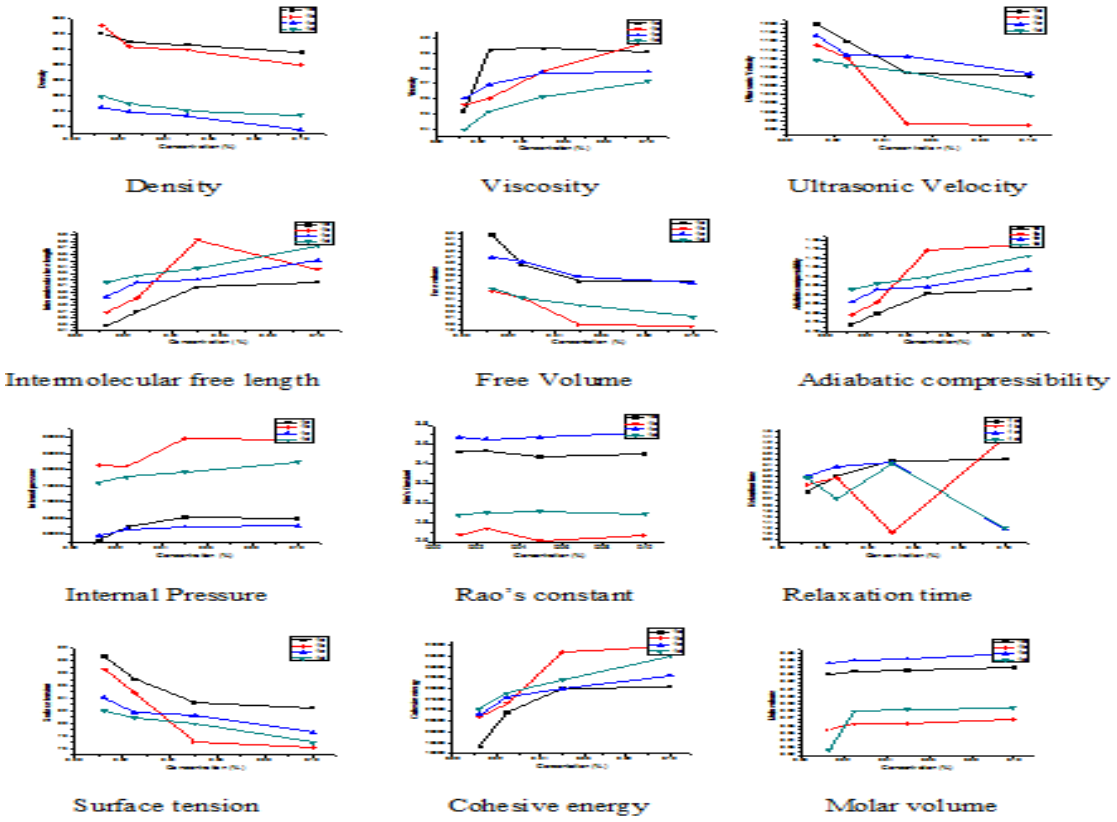


Fig.1.Variation of Density, Viscosity, Ultrasonic velocity, Intermolecular free length, Free volume, Adiabatic compressibility, Internal pressure, Rao's constant, Relaxation time, Surface tension, Cohesive energy, Molar volume With concentration .

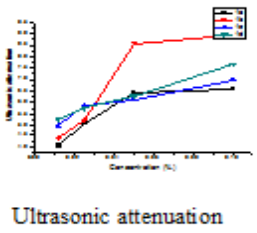


Fig.2.Variation of ultrasonic attenuation with concentration

Conclusion

In conclusion, we have used $LiOH{\cdot}H_2O$ as a catalyst for condensation of aryl aldehydes for an easy and highly efficient synthesis of chalcones. The advantages are (i) use of cheap and easily available catalyst, (ii) requirement of small amount (10 mol%) of the catalyst, (iii) room temperature reaction, (iv) short reaction times, (v) high product yields and (iv) clean product. In the present paper the ultrasonic velocity (v), density (ρ) and viscosity (η) and acoustical parameters viz. adiabatic compressibility(β_{ad}),intermolecular free length(L_f) , relaxation time (ζ)),free volume (V_f),internal pressure (Π_i),acoustic impedence(Z), surface tension(S), attenuation(a/f^2),Rao's constant(R),molar volume(V_m),cohesive energy(CE) have been measured for the compounds at different concentrations. The results obtained in this study showed that there is presence of specific molecular interactions in ethanol and chalcone molecules, which are responsible to increase absorption and transmission. Hence it is concluded that the association in these mixtures is the result of hydrogen bonding insolution.It may be concluded that the solute solvent interaction seems to be significant in system studied.

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