Synthesis, acoustical and thermodynamic properties of 3-phenyl-1-(2,4-difluorophenyl) prop-2-en-1-one in binary liquid mixtures at 298k

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ABSTRACT

3-phenyl-1- (2, 4-difluorophenyl) prop-2-en-1-one was synthesized and its characterization was done by MP, TLC, IR, H^1NMR, and Mass Spectra. The ultrasonic velocities, densities and viscosities in various compositions of methanol and benzene from 0-100% (by wt.) have been measured at 298K.

The experimental data was used for the determination of various thermodynamic parameters such as specific acoustical impedance (Z), intermolecular free path length (L_f), adiabatic compressibility (β), relaxation time (τ), absorption coefficient, solvation number (Sn), absorption coefficient values$\left(\frac{\alpha}{f^2}\right)$, and Gibb's free energy (ΔG) and The results showed that the presence of molecular interaction in the present system and obtained results were interpreted in terms of solute-solute and solute-solvent interactions in these solutions.

Keywords: Ultrasonic velocity, Thermodynamic properties, Acoustical impedance, Intermolecular free path length, Gibb's free energy

INTRODUCTION

Liquid and liquid mixtures have found wide applications in chemical, textile, leather & nuclear industries the study and understanding the thermodynamic and transport properties of liquid mixtures and solutions are more essential for their applications in industries. Various chalcones were synthesized by many researchers (Palepu *et al.*,1985; Comelli, 1995; Alonso *et al*,.2010; Alonso *et al.*, 2010; Alonso *et al.*,2011) they are known to exhibit various biological properties viz. antimalarial, antifungal, antibacterial anti-inflammatory, antituberculosis activity. The knowledge of the thermodynamic and acoustical properties of liquid mixtures with chalcones is of immense importance for understanding the molecular interactions between the components. Many co-workers (Hansen *et al.*, 1947; Kawaizumi *et al.*, 1977; Raso *et al.*, 1982; Fermeglla *et.al.*, 1990; Weiping *et al.*, 1992; Kumar *et al.*, 2011) studied acoustical properties in different aqueous and non-aqueous systems at different temperature by varying concentrations and in different % of organic solvents. In the present study the acoustical properties of 3-

phenyl-1- (2, 4-difluorophenyl) prop-2-en-1-one in methanol and benzene mixtures was measured. The results were interpreted in terms of molecular interactions.

SYNTHESIS

A mixture of 2, 4-difluoroacetophenone (10mmol) and benzaldehyde (10mmol) was stirred for 24 hours in presence of NaOH as a catalyst the product was isolated and recrystallized from ethanol. The purity of compound was checked by Thin Layer chromatography, Melting point, and the characterization of synthesized compound was done by IR, H^1NMR and Mass (GCMS).

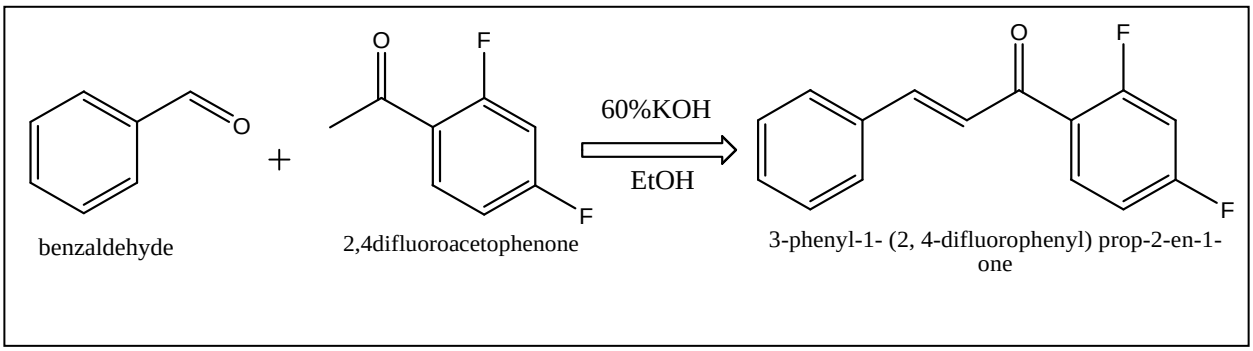

Fig 1: Structure of synthesized compound along with its IUPAC Name

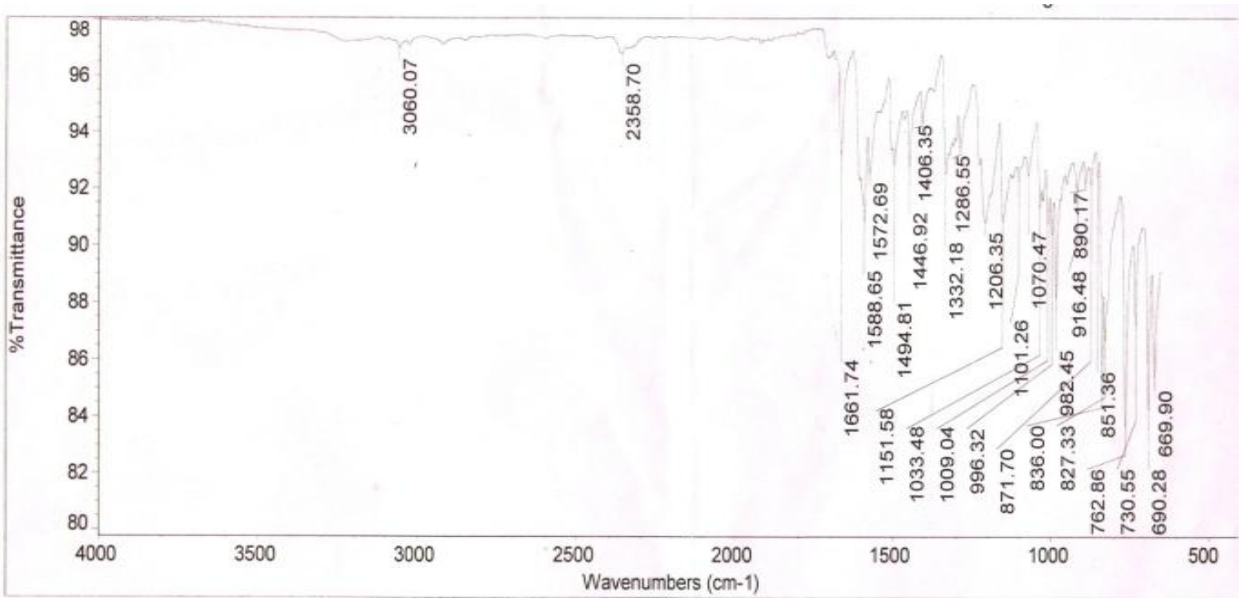

Fig 2: IR Spectra of synthesized compound

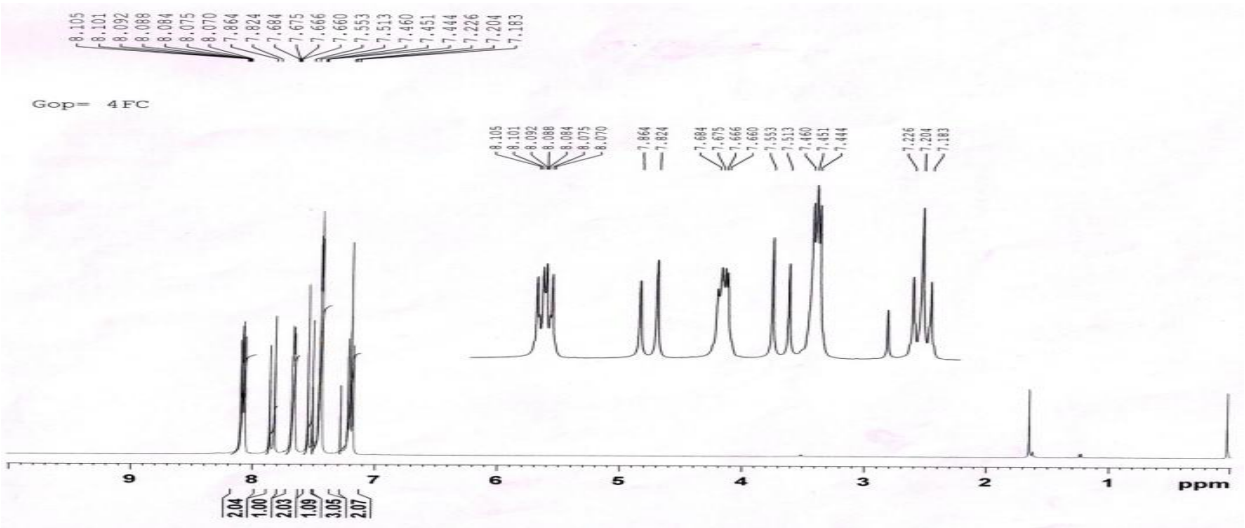

Fig 3: H1NMR Spectra of synthesized compound

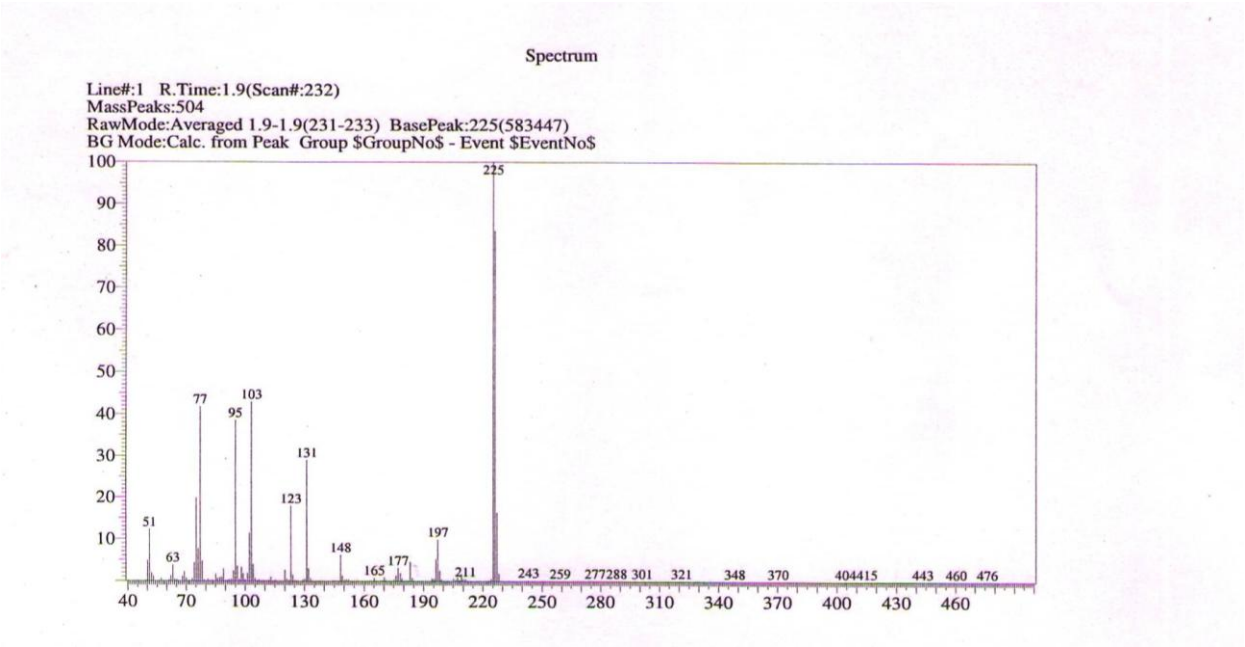

Fig 4: Mass Spectra of synthesized compound

MATERIALS AND METHODS

The chemicals used were of analytical grade and obtained from E. Merk, Thomas Baker Company Thermostatically controlled well-stirred water bath whose temperature was maintained to ±0.01K accuracy was used for all the measurements. Binary mixtures were prepared by weighing in airtight

bottles; the possible uncertainty in the concentration is estimated to be less than 0.0001. Densities of pure components and their mixtures were determined using a pyknometer having accuracy $1x10^{-5}$ m^3. Ubblehode viscometer having capacity of 5ml has been used to measure the flow times of pure liquids and liquid mixtures and it was calibrated with pure benzene (density: 0.8738 g/cm^3) and doubly distilled water (density: 0.9970 g/cm^3) at different temperatures the flow time of pure liquid mixtures were repeated for three times. The uncertainty of viscosity was $\pm 0.005x10^{-3}$ mPas. Speed of sound was measured by using a variable path, single crystal interferometer for liquids, (Mittal Enterprises, New Delhi.) working at 2MHz frequency. The interferometer was calibrated using water. Measurement of speed of sound through medium was based on the accurate determination of the wavelength of ultrasonic waves of known frequency produced by quartz crystal in the measuring cell. The interferometer cell was filled with the test liquid mixtures and water was circulated around the measuring cell from a thermostat. The uncertainty was estimated to be 0.1m/s.

RESULTS AND DISSCUSSION

The determined values of density, viscosity and ultrasonic velocity were listed in table no.1.The density and ultrasonic velocity values decreases with increase in the weight percent of methanol, suggests, the decrease is due to some dispersive forces due to powerful molecular dispersions. The observed decreasing trend in ultrasonic velocity with mole fraction of methanol by addition of benzene such variations is supported by increase in adiabatic compressibility (β) with increase in percentage wt. of methanol due to dispersion of solvent molecules around the solute molecules. The decrease in ultrasonic velocity and increases in β and L_f with increase in percentage of methanol values suggests predominance of solute-solvent interactions such increase suggests the hydrogen bonded association of alcohols breaks up gradually with addition of benzene. The values of viscous relaxation time (τ) showed linear increase with increase in mole fraction indicates some specific interactions among the component at high percentage of methanol. The degree of interaction was calculated in terms of solvation number (Sn) using (Shakya *et al.,* 2011) equation the decrease in the Sn with weight percent of methanol suggests the presence of solute –solute interactions the positive values suggests the structure forming tendency in methanol and benzene. The increase in absorption coefficient values $\left(\frac{\alpha}{f^2}\right)$ with increase in weight percent of methanol indicates the molecular interaction increases with increase in methanol.

The Gibb's free energy is found to decrease with weight percentage of methanol that is it shows negative deviation which suggests the dispersion forces are present with the system and these values were listed in table 2.

Table 1: Density, Viscosity, Refractive index, Ultrasonic velocity and Acoustical parameters of 3-phenyl-1- (2, 4-difluorophenyl) prop-2-en-1-one in methanol + benzene mixtures.

Wt. % of methanol	Density (ρ) g cm^{-3}	Viscosity (η) c.p	Refractive Index (n)	Ultrasonic velocity (U) ms^{-1}	Acoustical impedance (Z) $Kg.m^{-2}s^{-1}$	Adiabatic compressibility (β) × 10^{-7} $Kg^{-1}ms^{-2}$	Free path length(Lf)× 10^{-9} m
0	0.8690	0.6470	1.4915	1303.60	1132.8	6.772	50.045
10	0.8601	1.0828	1.4645	1250.66	1152.2	6.478	48.948
20	0.8529	1.1104	1.4510	1234.66	1052.1	7.691	53.335
30	0.8465	1.1059	1.4360	1217.77	1030.8	7.966	54.280
40	0.8408	1.1055	1.4240	1198.12	1007.4	8.285	55.356
50	0.8331	1.1009	1.4085	1188.88	990.48	8.492	56.043
60	0.8263	1.1025	1.3960	1184.00	978.37	8.633	56.500
70	0.8195	1.0820	1.3820	1163.35	953.42	9.016	57.746
80	0.8131	1.0689	1.3695	1154.22	945.95	9.231	58.432
90	0.8056	1.0312	1.3550	1137.77	916.59	9.589	59.553
100	0.7889	0.9791	1.3270	1111.55	876.92	10.26	61.600

Table 2: Thermodynamic Parameters of 3-phenyl-1- (2, 4-difluorophenyl) prop-2-en-1-one in methanol + benzene mixtures at 298K

Wt.% of methanol	Effective Molecular Weight (M_{eff})	Wada's constant(W)×10^{-3}	Absorption coefficient $\left(\frac{\alpha}{f^2}\right)$ ×$10^{-5}m^{-1}s^2$	Viscous relaxation time (τ) x10^{-7}s	Solvation Number (Sn) x10^6	Gibb's Free Energy (ΔG) × 10^{-7} J/mole
0	78.000	109.08	1.5436	7.8280	31.120	- 4.9977
10	68.900	99.531	2.2450	10.743	27.489	- 4.4938
20	61.587	26.036	2.3162	11.387	24.573	- 4.4011
30	55.578	73.563	2.4081	11.746	22.174	- 4.3517
40	50.555	66.055	2.4580	12.212	20.169	- 4.2897
50	46.293	60.297	2.4665	12.465	18.469	- 4.2571
60	42.628	55.523	2.5024	12.690	17.007	- 4.2286
70	39.447	50.275	2.5645	13.005	15.738	- 4.1896
80	36.660	46.925	2.5943	13.156	14.626	- 4.1712
90	34.194	43.345	2.6000	13.184	13.642	- 4.1679
100	32.000	40.046	2.6409	13.393	12.767	- 4.1428

FORMULAE

Various parameters such as adiabatic compressibility (β) free path length (L_f) and acoustical impedance (Z) were calculated from the measured data using the following standard expressions (Michael *et al.*, 1988; Natrajan *et al.*, 2011; Kaur *et al.*, 2015; Chavan *et al.*, 2016)

$$\textit{Adiabatic compressibility } (\beta) = \frac{1}{U^2 \times \rho}$$

$$\textit{Intermolecular Free path length} (L_f) = K_j \times \beta^{1/2}$$

Where, Kj= Jacobson's constant= 6.0816×10^4

$$\textit{Acoustical Impedance } (Z) = U \times \rho$$

By using the density, viscosity, and sound velocity some thermodynamic parameters were determined by following relations

Effective molecular mass(M_{eff}),

$$M_{eff} = \sum XiMi$$

Where, Xi= Mole fraction and Mi = molecular weight of i^{th} component.

The Molar compressibility or Wada's constant (Singh.C et.al 2014) can be calculated by equation,

$$W = \frac{M}{\rho} \times \beta^{-\frac{1}{7}}$$

Where, M = relative molar mass and β = compressibility factor.

The Absorption coefficient (Kannappan.V et.al 2014) was calculated by equation,

$$\left(\frac{\alpha}{f^2}\right) = \left(\frac{8\alpha\pi^2\eta}{3\rho U^2}\right)$$

Where, η = is the viscosity of the mixture, ρ= density of the mixture

The viscous relaxation time (τ) was calculated by equation,

$$\tau = \frac{4\eta}{3\rho U^2}$$

The Solvation number (Sn) can be calculated by equation,

$$Sn = M/Mo\left\{1 - \left(\frac{\beta}{\beta o}\right)\left(\frac{100-x}{x}\right)\right\}$$

Where M and Mo are the molecular weights of solvent and solute respectively β and βo are adiabatic compressibility of solvent and solution respectively and x is number of grams of compound in 100 gm. of solution.

The Gibb's free energy can be calculated by the equation,

$$\Delta G = KTlog\left[\frac{KT\tau}{h}\right]$$

Where, K is Boltzmann constant =1.23×10^{-23}J/K, $h$is Planks constant =6.626×10^{-26}Js

τ relaxation time = 4/3ηβ

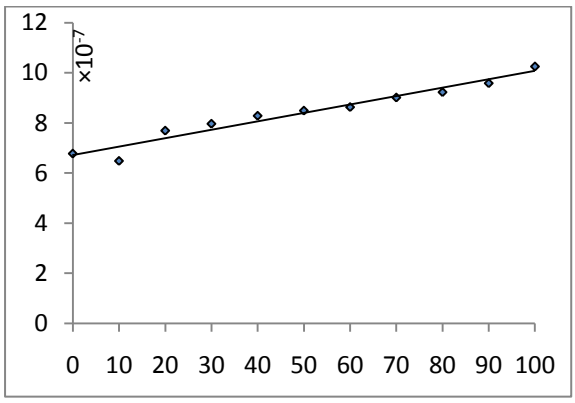

Fig 1: Relation between adiabatic compressibility and % composition of methanol

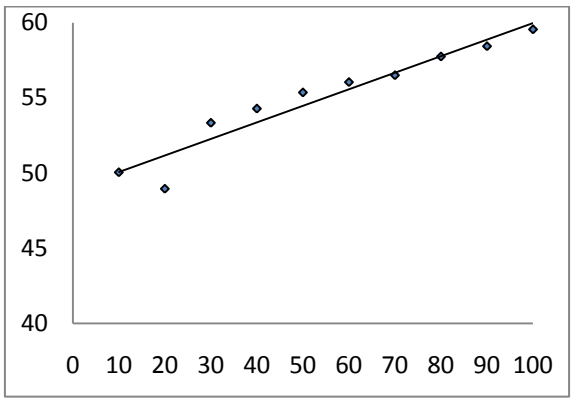

Fig 2: Relation between Free path Length and % composition of methanol

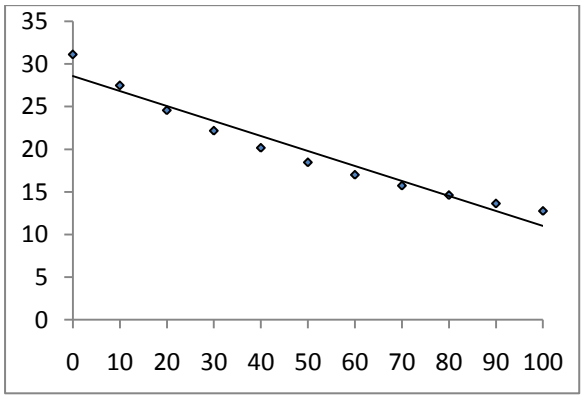

Fig 3: Relation between Solvation number and % composition of methanol

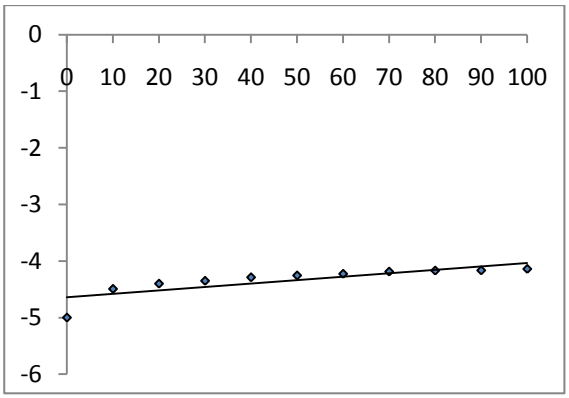

Fig 4: Relation between Free Energy and % composition of methanol

CONCLUSION

The acoustical parameters gives valuable information to understand the solute-solvent interactions in the binary solvent system; it showed that molecular interactions resulted in structure forming as judged on the basis of positive values of solvation number. The studied various thermodynamic parameters supports the existence of weak and strong dispersive forces in this binary mixtures and these changes are interpreted with the help of graphs Fig 1, Fig 2, Fig 3 and Fig 4.

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