SYNTHESIS, CHARACTERISATION AND STUDY OF THERMODYNAMIC PROPERTIES OF 1-(2,4-DICHLOROPHENYL)-3-(NAPTHALEN-1-YL)-2-PROPEN-1-ONE

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Abstract: In this study, 1-(2,4-dichlorophenyl)-3-(napthalen-1-yl)-2-propen-1-one was synthesized and characterised by FT-IR and ^{1}HNMR. The various concentrations (ranging from 0.01M to 0.1 M) of its solutions in DMF were prepared. Density, viscosity and ultrasonic velocity measurements of pure solvent and solutions were carried out at DMF at 288.15 K, 293.15 K, 298.15 K and 303.15 K. These measured data were used to determine thermodynamic parameters such as isentropic compressibility (β), intermolecular free pathlength (L_f), acoustic impedance (Z), Relaxation Strength (r), Molar compressibility (W), Apparent molar volume (ϕ_V), Apparent molar compressibility (ϕ_β), Solvation number (S_n), Free Volume (V_f), Internal Pressure (π) and Gibbs free energy (ΔG). Using these experimental data, various acoustical parameters have been calculated, which were interpreted in terms of solute-solute and solute-solvent interactions in solutions.

Key words: 1-(2,4-dichlorophenyl)-3-(napthalen-1-yl)-2-propen-1-one, ultrasonic velocity, viscosity, acoustical parameters, Gibb's free energy, solute solvent interaction.

I. INTRODUCTION

Naphthalene derivatives are medicinally important and exhibits anti-inflammatory, antimicrobial, antifungal and antioxidant properties [1]-[3]. Chalcones are the important constituent of many natural sources and have variety of biological activities. Chalcones have been reported to possess many useful properties, including anti-inflammatory, antimicrobial, antifungal, antioxidant, cytotoxic, antitumor and anticancer, antimalarial, antidiabetic activities [4]. The presence of α, β unsaturated ketone group in chalcone is responsible for their different activities [5]. Owing to the importance of the above, chalcone derived from naphthalene were chosen for the study of solute solvent interaction.

Ultrasonic interferometric measurements play an important role in medicinal chemistry as it helps for the study of pharmacokinetics and pharmacodynamics. The aim of carrying out this research is to study the drug suitability by studying the solute solvent interaction by viscometric and interferometric methods. The values of ultrasonic velocity, density, viscosity and adiabatic compressibility as a function of concentration will be of much help in providing about the types of bonds, type of molecular interactions, etc [6]-[17]. In order to understand the nature of molecular interaction between solute and solvent, it is of interest to calculate the acoustical parameters. Further, such studies as a function of concentration are useful in gaining insight into the structure and bonding of associated molecular complexes and other molecular processes.

In the present study density, viscosity and ultrasonic velocity measurement of 1-(2,4-dichlorophenyl)-3-(napthalen-1-yl)-2-propen-1-one in dimethylformamide (DMF) were carried out at 288.15 K, 293.15 K, 298.15 K and 303.15 K with a view to understand the molecular interactions in this solution.

II. MATERIALS AND METHODS

2.1 Synthesis of 1-(2,4-dichlorophenyl)-3-(napthalen-1-yl)-2-propen-1-one

To a mixture of 2,4-Dichloroacetophenone (0.01 mole) and 1-naphthaldehyde (0.01 mole) in ethanol (50 ml), 15 ml of 10% sodium hydroxide was added dropwise. The mixture was allowed to stand at 60°C with stirring for 6 to 8 hrs. The reaction mixture was kept for overnight and acidified with glacial acetic acid. The precipitated crystals were collected by filtration, washed with water and recrystallized from DMF (yield: 76% and m.pt. 132°C) [18]. The reaction scheme of the compound is shown in Fig.1

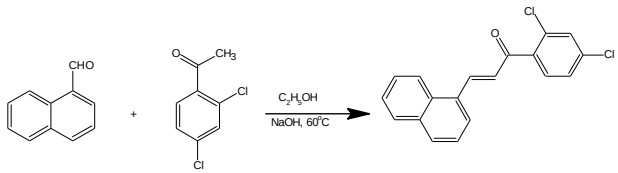


Fig. 1: Reaction scheme

2.2 Spectral Characterisation

The ^{1}H NMR spectrum was recorded by BRUKER Spectrometer (400 MHz) using internal reference TMS and solvent DMSO. Fig. 2 shows ^{1}H NMR spectrum of 1-(2,4-dichlorophenyl)-3-(napthalen-1-yl)-2-propen-1-one.

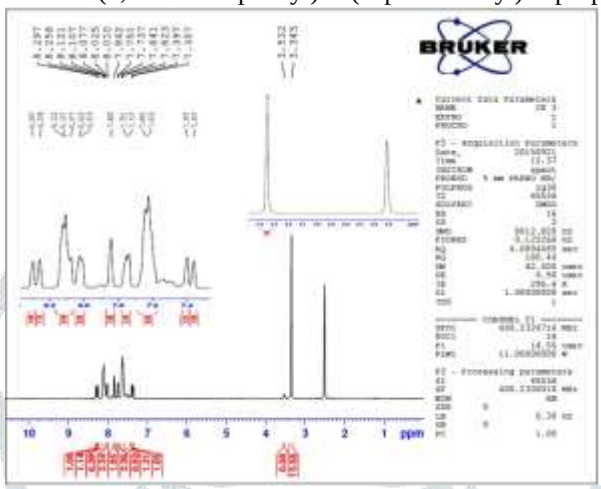


Fig. 2: ^{1}H NMR spectrum of 1-(2,4-dichlorophenyl)-3-(napthalen-1-yl)-2-propen-1-one

2.3 Study of Acoustical parameters

Ultrasonic velocities have been measured by using single crystal interferometer at a frequency of 3 MHz. The density and viscosity have also been measured by pycnometer and Ubbelhode viscometer. Using these experimental data, various acoustical parameters are calculated (see Sect. 2.3.3), which are interpreted in terms of solute-solute and solute-solvent interactions in different solutions. The solvent DMF used in the present work was of AR grade and was purified. The calculations of acoustical properties require the measurements of ultrasonic velocity (U), viscosity (η) and density (ρ).

2.3.1 Density measurements

The weight of distilled water, DMF and solutions of 1-(2,4-dichlorophenyl)-3-(napthyl)-2 propen-1-one in DMF were measured at 288.15 K, 293.15 K, 298.15 K and 303.15 K by using pycnometer. The densities (ρ) were evaluated by using following equation (1)

$$\rho = \frac{w \times \rho_o}{w_o} \qquad (1)$$

where w is the weight of solution, w_0 is the weight of water and ρ_o is the density of water.

2.3.2 Viscosity Measurements

Viscosity of solution was measured by using Ubbelohde viscometer. The measured quantity of the solvent / solution was placed in the viscometer, which was suspended in a viscometer bath at desired temperature. 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 solvent sample, the viscosity of solutions was determined according to equation (2)

$$\eta = \frac{t\,\rho\eta_o}{t_o\rho_o} \qquad (2)$$

where t, t_o and η_o are the time of solution, solvent and viscosity of solvent respectively.

2.3.3 Sound velocity measurement

Ultrasonic interferometer (Mittal Enterprise, New Delhi, Model No. F-81) working at frequency of 1 and 3 MHz was used to determine sound velocity. The solvent / solution was filled in the measuring cell with quartz crystal and then micrometre was fixed. The circulation of water from the thermostat was made and test solvent / solution in the cell is allowed to thermally equilibrate. The micrometre 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) travelled by the micrometre for n=20, was read. The wave length (λ) was determined according to the equation (3).

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

(3)

The sound velocity (U) of solvent and solutions were calculated from the wavelength and frequency (F) according to equation (4)

$$U = \lambda F \quad (4)$$

where, F= 3 x 10^6 Hertz.

The following thermodynamic parameters are calculated by using following standard expressions

1. Isentropic compressibility (β):

$$\beta = \frac{1}{U^2 \rho} \quad (5)$$

2. Intermolecular free path length (L_f):

$$L_f = K_J \beta^{1/2} \quad (6)$$

where K_J is Jacobson constant (=2.0965 X 10^{-6})

3. Acoustic impedance (Z):

$$Z = U \times \rho \quad (7)$$

4. Relaxation Strength (r):

$$r = 1 - \left[\frac{U}{U_\infty}\right]^2 \quad (8)$$

where U_∞ = 1.6 x 10^5 cm.s^{-1}

5. Molar compressibility (*W*):

$$W = \frac{M}{\rho} \beta^{-1/7} \quad (9)$$

The apparent molecular weight (*M*) of the solution can be calculated as:

$$M = M_1 X_1 + M_2 X_2 \quad (10)$$

where X_1 and X_2 are weight fractions of solvent and solute, respectively. M_1 and M_2 are the molecular weights of the solvent and solute respectively.

6. Apparent molar volume (ϕ_V)

$$\phi_V = \frac{(\rho_o - \rho)1000}{m\rho\rho_o} + \frac{M}{\rho_o} \quad (11)$$

7. Apparent molar compressibility (ϕ_β)

$$\phi_\beta = \frac{(\beta\rho_o - \beta_o\rho)1000}{c\rho_o} + \frac{\beta_o M}{\rho_o} \quad (12)$$

where c is the molar concentration of solute and M is the molar mass of the solute.

8. Solvation number (S_n)

$$S_n = \frac{\beta}{\beta_o\left(\frac{M}{\rho_o}\right)} \quad (13)$$

9. Free Volume (V_f)

$$V_f = \left[\frac{MU}{K\eta}\right]^{3/2} \quad (14)$$

10. Internal Pressure (π)

$$\pi = \frac{P_f RT \rho^{2/3}\left[\frac{K\eta}{U}\right]}{M^{7/6}} \quad (15)$$

where P_f is the packing factor (=2), η is viscosity of solution and K is a constant (K =4.28 x 10^9)

11. Gibb's Free Energy (ΔG)

$$\Delta G = kT \ln\left(\frac{kT\tau}{h}\right) \quad (16)$$

where τ is the viscous relaxation time given by $\tau = \frac{4}{3}\beta\eta$, k is the Boltzmann constant and h is the Planck's constant.

III. Results and Discussion

The experimental data of density (ρ), viscosity (η) and sound velocity (U) of pure solvents and solutions of synthesized 1-(2,4-dichlorophenyl)-3-(napthalen-1-yl)-2-propen-1-one in DMF at 288.15 K, 293.15 K, 298.15 K and 303.15 K were measured. The experimental data of various concentrations of the solution at 298.15 K are given in Table 3.1and shown in fig 3.1(a). It is observed that ultrasound velocity and viscosity increase with increase of concentrations of solution. Also, the experimental data were measured at 288.15 K, 293.15 K, 298.15 K and 303.15 K by keeping the concentration of solution constant and are given in Table 3.2 and shown in fig 3.1(b). Ultrasonic velocity decreases with increase in temperature may be due to the weakening of intermolecular forces between the molecules. From these experimental data, various acoustical parameters were evaluated using equations (1) to (16) at 298.15 K. The calculated acoustical parameters are given in Tables 3.3. Figure 3.2 shows the variation of acoustical parameters with concentration in DMF. In fig.3.2, both isentropic compressibility (β) and the intermolecular free length (L_f) decreases continuously with increase of concentration of solutions. The decrease of L_f suggests that there is strong interaction between solvent and compound molecules. Free volume decreases with increase in mole fraction indicates intermolecular interaction seems to be stronger than the intramolecular interaction. Fig.3.2 shows increase of acoustic impedance (Z), Internal Pressure (π) and Gibbs free energy (ΔG) with increase of concentration. Z increases with increase in concentration indicates that there is an increase of molecular concentration. Gibbs free energy increases with increase in concentration of solution. This gives evidence for the strong interaction between solvent and solute molecules. The increase in Gibbs free energy also suggests shorter time for rearrangement of the solute molecules in the solution. Positive excess values of internal pressure represent the presence of dispersive forces between molecules.

Table 3.1 The density (ρ), ultrasonic velocity (U) and viscosity (η) at 298.15 K

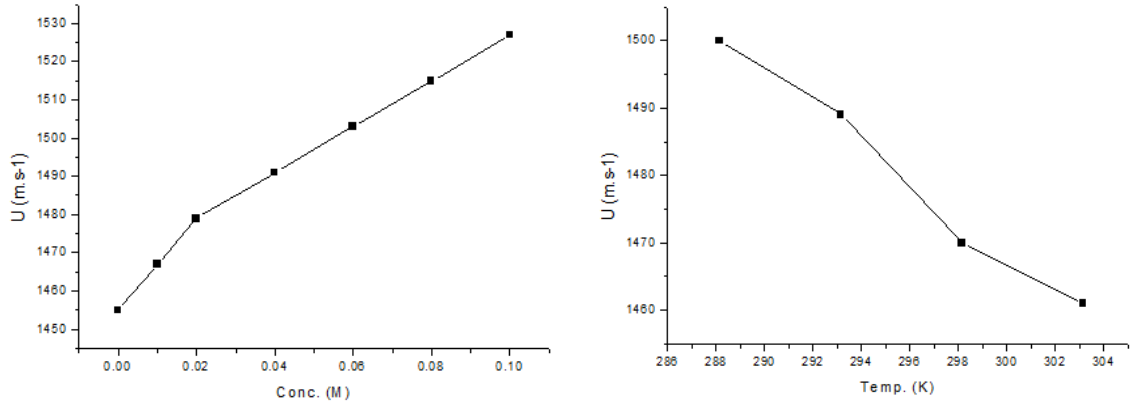
Conc. (M)	ρ kg.m^{-3}	U m.s^{-1}	η x 10^{-3} Nm^{-2}s
0.00	944.50	1455	0.8020
0.01	943.65	1467	0.8125
0.02	943.87	1479	0.8407
0.04	945.76	1491	0.8705
0.06	947.30	1503	0.9675
0.08	949.21	1515	1.0427
0.10	950.45	1527	1.0554

Table 3.2: The density (ρ), ultrasonic velocity (U) and viscosity (η) at 288.15, 293.15, 298.15 K and 303.15K

Temp.(K)	ρ kg.m^{-3}	U m.s^{-1}	η x 10^{-3} Nm^{-2}s^{-1}
288.15	0.94450	1500	0.8020
293.15	0.94365	1489	0.8125
298.15	0.94387	1470	0.8407
303.15	0.94576	1461	0.8705

Table 3.3: Various Acoustical parameters at 298.15K

Conc. (M)	β x10^{-10} m^{2}N^{-1}	L_f x10^{-11} m	Z x 10^{-6} Nm^{-2}	r	Wx10^{-3}	V_f x10^{-3} m^{3}mol^{-1}	π x 10^3 atm	ΔGx10^{-20} kJmol^{-1}	ϕ_V m^{3}mol^{-1}	ϕ_β m^{2}N^{-1}	S_n
0.00	5.0012	4.6885	1.3742	0.1730	7.3799	5.4432	1.5533	0.4938	-	-	
0.01	4.9241	4.6522	1.3843	0.1593	7.4029	5.4261	1.5512	0.4928	4.1164	-62.4862	-36.0883
0.02	4.8434	4.6139	1.3960	0.1455	7.4187	5.2385	1.5671	0.5000	4.1145	-21.8647	-12.6277
0.04	4.7562	4.5722	1.4101	0.1316	7.4231	5.0720	1.5807	0.5069	4.0981	-7.2253	-4.1729
0.06	4.6730	4.5320	1.4238	0.1176	7.4298	4.4174	1.6509	0.5431	4.0848	-0.4489	-0.2592
0.08	4.5900	4.4916	1.4381	0.1034	7.4338	4.0269	1.6989	0.5665	4.0684	1.1096	0.6408
0.10	4.5122	4.4534	1.4513	0.0892	7.4422	4.0331	1.6937	0.5645	4.0577	2.1436	1.2380



(a) (b)

Fig 3.1 Plot of (a) Ultrasonic velocity vs Concentration at 298.15 K, (b) Variation of Ultrasonic velocity with Temperature

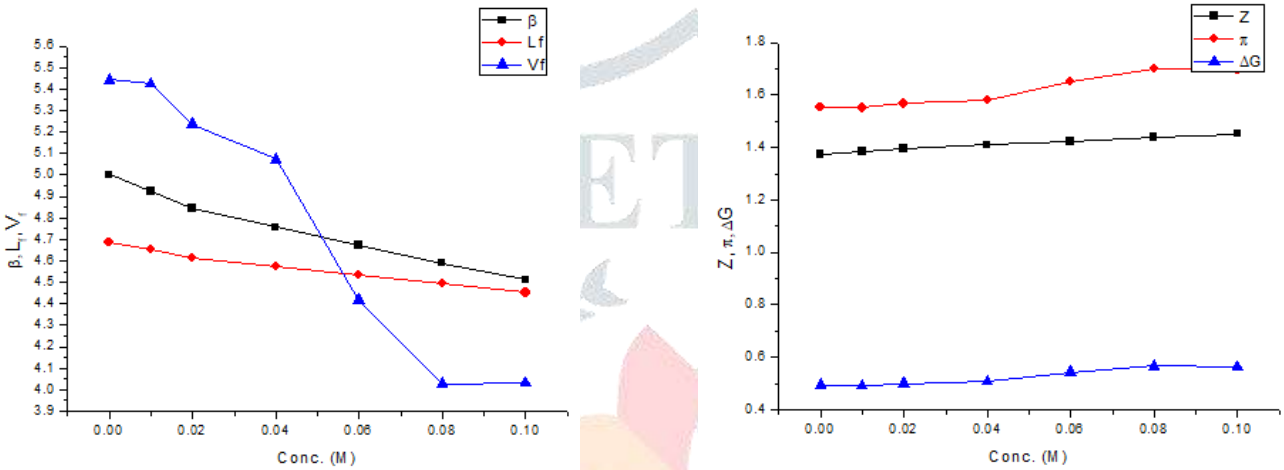


Fig 3.2 Variation of acoustical parameters with concentration at 298.15 K

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REFERENCES

1. U Ram Shankar,V Jaya Kishore, A Ramakant Kardile, V Santosh Lahore, S Shailesh Dixit, S Hemant Kumar Deokar, D Popat, P Shinde Manash, Sarmah Jyoti Chattopadhyaya, 2010. Novel quinoline and naphthalene derivatives as potent antimycobacterial agents. Eur. J. Med. Chem, 45,1854-1867.
2. Shafiea, S Emamic, S Ghodsid, S Najjaria, M Sorkhia, N Samadie, M A Faramarzie and A Foroumadia, 2009, Characterization, synthesis and biological evaluation of naphthalene based piperazines as antibacterial agents. J. Iran. Chem. Soc, 6(2), 325-333.
3. Banu Koz, D Serafettin, I Siddik, 2016. Synthesis and Properties of Alkyl chain substituted naphthalenetetracarboxylic monoanhydride monoimides and unsymmetrically substituted naphthalene derivatives, Asian Jour chem, 28(12), 2755-2758.
4. B A Bhat, K L Dhar, A K Saxena, M Shanmugavel, 2005. Synthesis and biological evaluation of chalcones and their derived pyrazoles as potential cytotoxic agents, Bioorg. Med. Chem., 15(3),177.
5. D N Dhar, 1981. The chemistry of chalcones and releted compounds, Wiley Interscience, New York.
6. A Ali, A K Nain, M Kamil, 1996. Physico-chemical studies of non-aqueous binary liquid mixtures at various temperatures. Thermochim. Acta 274, 209-221.
7. R L Kay, D F Evans and Sister M A Hatesich, 1976. Solute-solvent interactions, Ed. J. F, Coetzee and C. D. Ritchie, M. Dekker Inc. Publ., 2, 105.
8. J Manuel Bernal-Garca, Adriana Guzmn-Lpez,Alberto Cabrales-Torres, Alejandro Estrada-Baltazar and Gustavo A. Iglesias-Silva, 2008. Densities and Viscosities of (N,N-Dimethylformamide + Water) at Atmospheric Pressure from (283.15 to 353.15) K, J. Chem. Eng. Data 53, 1024-1027.
9. A Marchetti, C Preti, M Tagilazucchi, L Tassi, G Tosi, 1991. The N,N-Dimetlylformamide/ Ethane-1,2 diol Solvent System. Density, Viscosity, and Excess Molar Volume at Various Temperatures. J. Chem. Eng. Data, 36, 1442-1445
10. P Sharlin, K Steinby, U Domanska, 2002. Volumetric Properties of Binary Mixtures of N,N-Dimethylformamide with Water or Water-d2 at Temperatures from 277.13 to 318.15 K. J. Chem. Thermodyn, 34, 927-957.
11. S Baluja, D Lava, 2017. Ultrasonic behavior of various chalcones in some solvents at di_erent temperatures, Rev. Colomb. Cienc. Qum. Farm., 45(3), 339-361.

12. B Jacobson, A Anderson, J Arnold, 1954. A Proton magnetic resonance study of the hydration of deoxyribonucleic acid, Nature (London), 173, 772-773.
13. R Palani, A Geetha, 2009. Acoustical and excess thermodynamic studies of molecular interaction in aqueous mixed solvent systems at 303, 308 and 313 K, Phys. Chem.Liq., 47, 542-552.
14. R Gajera, R Bhalodia, S Baluja, 2009. International Journal of Applied Chemistry, 5,47-55.
15. A Kulshrestha, S Baluja, 2010. Synthesis and acoustical studies of some chalcones of furaldehyde in di_erent solvents at 308.15K, Advances in Applied Science Research, 1 (3): 229-239.
16. M Praharaj, P Mishra, S Mishra, A Satapathy, 2012. Study of thermodynamic and transport properties of ternary liquid mixture at di_erent temperatures, Advances in Applied Science Research, 3(3),1518-1530.
17. A B Naik, 2015. Densities, viscosities, speed of sound and some acoustical parameter studies of substituted pyrazoline compounds at di_erent temperatures, Ind. J. Pure & Applied Physics, 53, 27-34.
18. B Shivarama Holla, B Kalluraya and K.R. Sridhar, 1987. Synthesis of Some 1-Aryl-3-(5- nitro-2- furyl)- 2-propen- 1-ones as potential Antibacterial Agents. Current Science, 56, 585- 588.