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# Effect of temperature and solvents on ultrasonic velocity and thermodynamic parameters of 1,3,4-oxadiazole derivative solutions

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#### A R T I C L E I N F O

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#### ABSTRACT

The present work describes the synthesis, characterization, thermal analysis and physico-chemical parameters of 2-((4-acetyl-5-methyl-5-phenyl-4,5-dihydro-1,3,4-oxadiazol-2-yl)methylthio)-3-o-tolylquinazolin-4(*3H*)-one (PD<sub>I-H</sub>). The compound PD<sub>I-H</sub> is synthesized by using standard protocols; purity is monitored by using TLC and characterized by IR and NMR spectral techniques. The thermal behavior of PD<sub>I-H</sub> was studied by TGA and DTA techniques at a heating rate of 10 °C/min in nitrogen atmosphere. Thermal stability and kinetic parameters were determined according to the Freeman–Anderson method. The density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity (*U*) of pure solvents (chloroform (CF), *N,N*-dimethyl formamide (DMF)) and solutions of PD<sub>I-H</sub> (0.01–0.001 M) in CF and DMF were investigated at three different temperatures: 303 K, 308 K and 313 K. Using  $\rho$ ,  $\eta$  and *U* data various thermodynamic parameters such as adiabatic compressibility ( $\kappa_a$ ), intermolecular free path length ( $L_f$ ), Rao's molar sound function ( $R_m$ ), Van der Waals constant (b), internal pressure ( $\pi$ ), free volume ( $V_f$ ) and solution number ( $S_n$ ) were calculated. The results obtained were interpreted in terms of solute–solvent and solute–solute interactions. The structure making or structure-breaking abilities of the solute in CF and DMF solvent were also studied.

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#### 1. Introduction

Ultrasonic is a subject of extensive research and as its usefulness in the fields of biology, biochemistry, engineering, geography, geology, medicine and polymer industry is found very interesting [1,2]. Ultrasonic has also been applied to process monitoring and materials characterization [3]. Ultrasonic velocity (*U*) together with density ( $\rho$ ) and viscosity ( $\eta$ ) data furnishes a wealth of information about bulk properties and intermolecular forces [4,5], which find applications in several industries and technological processes. A literature survey reveals that ultrasonic velocity of various organic, inorganic and biological compounds in various solvents have been studied [6–9]. Our research group has also studied acoustical properties of synthesized compounds in various solvents [10,11].

2,5-Disubstituted-1,3,4-oxadiazole derivatives are known for various pharmacological activities such as antibacterial [12], anti-inflammatory [13], analgesic [14], antiviral and anticancer [15], antihypertensive [16], anticonvulsant [17], antiproliferative [18,19], herbicidal [20], hypoglycemic [21], hypnotic and sedative [22], MAO inhibitor [23] and insecticidal [24].

The choice of 1,3,4-oxadiazole is due to its multi-applicability in the field of medicine. It is an important moiety in the drug industry. The applications of these compounds attract us to study their behavior in various solvents and also investigate their thermodynamic and

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chemical kinetic parameters. In this context, the present paper describes the synthesis, characterization, thermal analysis and physicochemical parameters of 2-((4-acetyl-5-methyl-5-phenyl-4,5-dihydro-1,3,4-oxadiazol-2-yl)methylthio)-3-o-tolylquinazolin-4(*3H*)-one (PD<sub>I-H</sub>). In continuation of our research work, the present work deals with acoustical properties of newly synthesized 1,3,4-oxadiazole derivative in chloroform (CF) and *N*,*N*-dimethyl formamide (DMF) solvents.

#### 2. Experimental

#### 2.1. Materials

The 2-((4-acetyl-5-methyl-5-phenyl-4,5-dihydro-1,3,4-oxadiazol-2-yl)methylthio)-3-o-tolylquinazolin-4(*3H*)-one (PD<sub>I-H</sub>) used in this study was synthesized in our laboratory. The molecular weight of PD<sub>I-H</sub> is 484.16. The structure of the present synthesized new PD<sub>I-H</sub> is shown in Fig. 1. The solvents: chloroform (CF) and *N*,*N*-dimethyl formamide (DMF) used in the present study were of A R grade and were purified according to literature methods [25]. The estimated purity of solvents was more than 99.8% and was confirmed by HPLC. The schiff-base of (Z)-N'-benzylidene-2-(4-oxo-3-o-tolyl-3,4-dihydroquinazolin-2-ylthio)acetohydrazide was synthesized in our laboratory [26]. The 1,3,4-oxadiazole derivative of 2-((4-acetyl-5-methyl-5-phenyl-4,5-dihydro-1,3,4-oxadiazol-2-yl)methylthio)-3-o-tolyl-quinazolin-4(*3H*)-one (PD<sub>I-H</sub>) was synthesized by reacting schiff-base with acetic anhydride and was purified three times from chloroform–nhexane prior to its use.

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Fig. 1. Structure of 2-((4-acetyl-5-methyl-5-phenyl-4,5-dihydro-1,3,4-oxadiazol-2-yl)methylthio)-3-o-tolylquinazolin-4(3H)-one (PD<sub>I-H</sub>).

## 2.2. Synthesis of 2-((4-acetyl-5-methyl-5-phenyl-4,5-dihydro-1,3,4-oxadiazol-2-yl)methylthio)-3-o-tolylquinazolin-4(3H)-one (PD<sub>I-H</sub>)

A mixture of Schiff-base 0.005 mol (2.15 g) and acetic anhydride (10 mL) were taken into a 100 mL round bottom flask and was refluxed for 4 h in oil bath. The progress of the reaction was monitored with the aid of TLC. The excess of acetic anhydride was then distilled off and the remaining mixture was poured in ice cold water to form yellowish solid compound PD<sub>I-H</sub>. The product was separated by filtration and crystallized from chloroform–n-hexane to afford the title compound PD<sub>I-H</sub>. The purity of the compound was checked by aluminum coated TLC plates  $60F_{245}$  (E. Merck) and the compound is purified by column chromatography using silica gel (60–120 mesh) and chloroform:n-hexane as an eluent. Yield–72%, m.p. 322 °C, Anal.

calc. for  $C_{27}H_{24}N_4O_3S:C-66.92$ ; H-4.99; N-11.56. Found: C-66.87; H. 4.94; N, 11.57%.

An IR spectrum of  $PD_{I-H}$  was recorded over the range of 4000–400 cm<sup>-1</sup> using FT-IR-thermonicolate IR 200 spectrophotometer. Sample for IR spectra measurement was prepared by KBr disk method. <sup>1</sup>H NMR spectrum was recorded using Brucker DRX 300 in CDCl<sub>3</sub> at 200 MHz with reference to TMS as an internal standard. Elemental analysis was performed by a Perkin-Elmer 2400-CHN analyzer and a melting point was recorded on a Gallenkemp apparatus.

#### 2.3. Thermal study

Thermal analysis (TGA/DTA) was carried out using a Mettler-Toledo, TGA/SDTA 851e instrument in flowing nitrogen or argon (flow



Fig. 2. IR spectrum of PD<sub>I-H</sub>.



Fig. 3. <sup>1</sup>H NMR spectrum of PD<sub>I-H</sub>.

rate = 50 mL/min), at a heating rate of 10  $^{\circ}$ C/min, and the data were processed using STARe software.

#### 2.4. Measurements of density, viscosity and ultrasonic velocity

#### 2.4.1. Apparatus and procedure

All the samples were prepared freshly and retained at the desired temperature for 24 h, to ensure their solubility at the temperature. Samples were kept in bottles with PTFE septum under vacuum until further use.

2.4.2. Density, viscosity and ultrasonic velocity

Ultrasonic velocity, density and viscosity measurements in pure solvents (CF and DMF) and solutions of compound  $PD_{I-H}$  (0.001–0.010 mol L<sup>-1</sup>) in CF and DMF were made at three different temperatures: 303 K, 308 K and 313 K, by using a M-81 multifrequency ultrasonic interferometer (2 MHz) (Mittal Enterprise, New Delhi), a Single Capillary Pycnometer made of borosil glass having a bulb capacity of 10 mL and an Ubbelohde viscometer. The Ubbelohde viscometer with 25 mL capacity was used for the viscosity measurement. The Ubbelohde viscometer was calibrated with fresh conductivity water immersed in a



Fig. 4. TGA and DTA curves of PD<sub>I-H</sub>.



Fig. 5. The Anderson-Freeman plot for thermal degradation of PD<sub>I-H</sub>.

water bath that was maintained at the experimental temperature. The flow time of water (t<sub>w</sub>) and the flow time of solution (t<sub>s</sub>) were measured with a digital stop clock with an accuracy of  $\pm 0.01$  s (Model: RACER HS-10W). Ultrasonic velocity (*U*), density ( $\rho$ ) and viscosity ( $\eta$ ) measurements were accurate to  $\pm 0.2\%$ ,  $\pm 0.1$  kg m<sup>-3</sup> and  $\pm 0.1\%$ , respectively. The uncertainty of temperature is  $\pm 0.1$  K and that of concentration measured is  $\pm 0.0001$  mol dm<sup>-3</sup>.

Theoretical equations:

From the experimental data of density, viscosity and ultrasonic velocity, various acoustical parameters are evaluated using standard equations:

Adiabatic compressibility : 
$$\kappa_a = 1/U^2 \rho$$
 (1)

Rao's molar sound function [27]:  $R_m = (M/\rho)U^{1/3}$  (2)

where *M* is the apparent molecular weight of solution and can be calculated according to the following equation:  $M = M_1W_1 + M_2W_2$  where  $W_1$  and  $W_2$  are weight fractions of solvent and solute, respectively.  $M_1$  and  $M_2$  are molecular weights of the solvent and solute, respectively.

Van der Waals constant [28]:

$$b = M/\rho \left\{ 1 - \left[ RT/\left( MU^2 \right) \right] \left[ \sqrt{\left( 1 + \left( MU^2 \right)/3RT \right) - 1} \right] \right\}$$
(3)

where *R* (8.3143 J K<sup>-1</sup> mol<sup>-1</sup>) is the gas constant and *T* (*K*) is absolute temperature.

Table 1
Comparison of measured density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity (U) data for
pure CF and DMF with literature values at 303, 308 and 313 K.

Organic	Experimental			Literature		
liquids	303 K	308 K	313 K	303 K	308 K	313 K
	ho (kg m	<sup>-3</sup> )		ho (kg m <sup>-3</sup> )		
CF	1475.3	1470.8	1465.8	1475.4 [34]	1472.7 [34]	1467.6 [34]
DMF	941.7	937.2	933.6	939.7 [35]	936.8 [38]	929.8 [41]
	$\eta$ (m Pa	s)		$\eta$ (m Pa s)		
CF	0.6628	0.6279	0.5781	0.6080 [37]	0.6393 [39]	0.5460 [37]
DMF	0.7588	0.7056	0.6353	0.7520 [36]	0.7070 [36]	0.6641 [36]
	$U (m s^{-})$	<sup>1</sup> )		$U (m s^{-1})$		
CF	960.0	950.8	932.4	959.0 [37]	949.6 [34]	933.6 [34]
DMF	1442.0	1432.0	1402.0	1446 [40]	1426 [40]	1404 [40]

#### Table 2

The density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity (U) of PD<sub>I-H</sub> in CF and DMF at 303, 308 and 313 K.

Conc.	$Chloroform + PD_{I-H} \ system$			DMF + PD <sub>I-H</sub> system		
$(mol L^{-1})$	Density (kg m <sup>-3</sup> )	Viscosity (m Pa s)	Velocity $(m s^{-1})$	Density (kg m <sup>-3</sup> )	Viscosity (m Pa s)	Velocity $(m s^{-1})$
	303 K			303 K		
0.000	1475.3	0.6628	960.0	941.7	0.7588	1442.0
0.001	1475.9	0.6642	963.2	942.2	0.7605	1444.8
0.002	1476.1	0.6650	964.4	942.4	0.7618	1445.2
0.004	1476.4	0.6663	966.4	942.5	0.7646	1446.4
0.006	1476.5	0.6679	967.2	942.8	0.7670	1447.6
0.008	1476.9	0.6692	968.8	943.1	0.7692	1449.6
0.010	1477.3	0.6705	973.2	943.8	0.7719	1455.2
	308 K			308 K		
0.000	1470.8	0.6279	950.8	937.2	0.7056	1432.0
0.001	1471.2	0.6292	953.2	938.3	0.7081	1434.8
0.002	1471.5	0.6300	954.0	938.5	0.7101	1436.0
0.004	1472.0	0.6317	954.8	938.7	0.7119	1436.8
0.006	1472.2	0.6333	956.0	939.0	0.7135	1438.4
0.008	1472.4	0.6344	957.6	939.4	0.7159	1440.8
0.010	1473.1	0.6362	960.8	940.5	0.7193	1446.0
	313 K			313 K		
0.000	1465.8	0.5781	932.4	933.6	0.6353	1402.0
0.001	1466.3	0.5793	934.8	934.2	0.6365	1404.0
0.002	1466.5	0.5804	935.6	934.3	0.6377	1404.8
0.004	1466.6	0.5818	936.0	934.6	0.6399	1406.0
0.006	1466.9	0.5833	937.6	934.9	0.6420	1407.6
0.008	1467.3	0.5848	938.8	935.1	0.6445	1409.2
0.010	1468.0	0.5868	942.0	935.7	0.6476	1412.0



**Fig. 6.** The plots of density ( $\rho$ ) against concentration (*C*) for PD<sub>I-H</sub> in (a) CF at 303 K ( $\blacklozenge$ ), 308 K ( $\blacksquare$ ) and 313 K ( $\blacktriangle$ ); (b) DMF at 303 K ( $\blacklozenge$ ), 308 K ( $\blacksquare$ ) and 313 K ( $\blacktriangle$ ).



**Fig. 7.** The plots of viscosity ( $\eta$ ) against concentration (*C*) for PD<sub>I-H</sub> in (a) CF at 303 K ( $\blacklozenge$ ), 308 K ( $\blacksquare$ ) and 313 K ( $\blacktriangle$ ); (b) in DMF at 303 K ( $\blacklozenge$ ), 308 K ( $\blacksquare$ ) and 313 K ( $\bigstar$ ).

Internal pressure [29]:  $\pi = b'RT (K\eta/U)^{1/2} (\rho^{2/3}/M^{7/6})$  (4)

where *R* (8.3143 J mol<sup>-1</sup> K<sup>-1</sup>) is the gas constant and b'(2) is the packing factor and *K* (4.28×10<sup>9</sup>) is a constant.

Solvation number : 
$$S_n = M_2/M_1[(1-\kappa_a)/\kappa_{a1}][(100-X)/X]$$
 (5)

where *X* is the number of grams of solute in 100 g of the solution.  $M_1$  and  $M_2$  are the molecular weights and  $\kappa_{a1}$  and  $\kappa_a$  are adiabatic compressibility of solvent and solute respectively.

Free volume [30]: 
$$V_f = [MU/K\eta]^{3/2}$$
 (6)

Intermolecular free path length [31]: 
$$L_f = \kappa_i \kappa_a^{1/2}$$
 (7)

where  $\kappa_j$  is a temperature-dependent Jacobson's constant (93.875 + 0.375 T) × 10<sup>-8</sup>.

#### 3. Results and discussions

#### 3.1. IR spectra

The IR spectrum of  $PD_{I-H}$  is depicted in Fig. 2. Spectra of  $PD_{I-H}$  were scanned over the frequency range of 4000–400 cm<sup>-1</sup>. The IR data of



**Fig 8.** The plots of velocity (*U*) against concentration (*C*) for PD<sub>I-H</sub> in (a) CF at 303 K ( $\blacklozenge$ ), 308 K ( $\blacksquare$ ) and 313 K ( $\blacktriangle$ ); (b) DMF at 303 K ( $\blacklozenge$ ), 308 K ( $\blacksquare$ ) and 313 K ( $\blacktriangle$ ).

synthesized 1,3,4-oxadiazole analogues clearly shows a C = N stretching band at 1685 cm<sup>-1</sup>, C–O absorption band at 1019 cm<sup>-1</sup> and C–N stretching band at 1275 cm<sup>-1</sup>, which confirmed ring closure of the 1,3,4-oxadiazole. IR absorption bands at 3077 cm<sup>-1</sup> and 1510 cm<sup>-1</sup> confirmed the presence of aromatic C–H and C = C in basic skeleton. The stretching band at 760 cm<sup>-1</sup> indicates the presence of 1,2-disubstituted and IR absorption band at 747 cm<sup>-1</sup> and 684 cm<sup>-1</sup> indicates the presence of monosubstituted benzene ring in synthesized compound. The bending vibration of –CH<sub>3</sub> and –CH<sub>2</sub> was observed at 1384 cm<sup>-1</sup> and 1477 cm<sup>-1</sup> respectively. The C–H symmetric stretching and asymmetric stretching absorption are observed at 2852 cm<sup>-1</sup> and 2923 cm<sup>-1</sup> respectively. All the IR group frequencies were suggestive that 1,3,4-oxadiazole derivative is prepared successfully.

#### 3.2. <sup>1</sup>H-NMR spectra

The proton NMR spectrum of PD<sub>1-H</sub> is depicted in Fig. 3. The peak due to residual CHCl<sub>3</sub> was observed at about 7.26  $\delta$ ppm either as a separate peak or overlapped with aromatic proton signals. It can be seen from the chemical structure of compound PD<sub>1-H</sub> that proton of the phenyl ring attached to the carbons C-d, C-f, C-I, C-g, C-m, C-m', C-n, C-n' and C-o appeared as a multiplet at 7.46–7.52  $\delta$ ppm. Chemical shift in the aromatic region with triplet at 7.56–7.59  $\delta$ ppm, 7.71–7.74  $\delta$ ppm and 7.98–8.02  $\delta$ ppm corresponds to C-h, C-b and C-c, respectively. The protons, which were present in methylene (C-j) (present in oxadiazole nucleus) and methyl group of C-e (attached to phenyl ring), both appeared as a singlet at 2.54  $\delta$ ppm. The other

Table 3

The	least-square equat	ions and regressio	n coefficients for I	PD <sub>I-H</sub> solutions	in CF at 30	3, 308 and 313 K.
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Parameter	Least square equations (regression coefficients	, $R^2$ ) [CF + PD <sub>I-H</sub> system]	
	303 K	308 K	313 K
ho (kg m <sup>-3</sup> )	146.0 C+1475.0 (0.976)	189.5 C+1471.0 (0.961)	173.7 C+1466.0 (0.930)
$\eta$ (m Pa s)	0.700 C + 0.663 (0.999)	0.765 C+0.628 (0.997)	0.801 C+0.578 (0.996)
$U (m s^{-1})$	986.3 C+962.1 (0.938)	774.7 C+952.0 (0.939)	732.0 C+933.6 (0.929)
$Z \times 10^{6} (\text{kg m}^{-2} \text{s}^{-1})$	1.597 C + 1.419 (0.943)	1.322 C+1.400 (0.949)	1.237 C+1.368 (0.929)
$\kappa_a \times 10^{-10} (Pa^{-1})$	-15.44 C+7.319 (0.943)	-12.97 C+7.499 (0.946)	-13.00  C + 7.824 (0.930)
$L_f \times 10^{-11} (m)$	-6.014  C + 5.664 (0.942)	-4.986 C+5.733 (0.946)	-4.891  C + 5.856 (0.930)
$R_m \times 10^{-4} (m^{10/3} s^{-1/3} mol^{-1})$	78544 $C^3$ – 1157.0 $C^2$ + 6.424 C + 7.988 (0.995)	191.3 C <sup>2</sup> - 0.778 C + 7.993 (0.994)	$19844 C^3 - 223.7 C^2 + 1.645 C + 7.965 (0.987)$
$b \times 10^{-5} (m^3)$	-0.553 C + 7.964 (0.963)	-0.808  C + 7.989 (0.942)	$-91.60 C^{2} + 0.257 C + 8.013 (0.986)$
$\pi \times 10^8$ (Pa)	$-69996 C^{3} + 1018 C^{2} - 3.471 C + 4.231$ (0.945)	$-172.7 C^{2}+2.955 C+4.125 (0.993)$	1.452 C+4.122 (0.968)
$V_f \times 10^{-7} (m^3)$ $S_n$	$\begin{array}{l} 13662\ C^3-1988.C^2+7.222\ C+2.570\ (0.942)\\ -3E+09\ C^4+4E+07\ C^3-19511\ C^2\\ +506.0\ C-0.183\ (0.993) \end{array}$	$\begin{array}{l} -1.468 \ C+2.308 \ (0.954) \\ 2E + 09 \ C^4 - 4E + 07 \ C^3 + 29830 \ C^2 \\ -398.2 \ C + 0.362 \ (0.987) \end{array}$	$\begin{array}{l} - 2.590 \ C + 3.024 \ (0.922) \\ - 1E + 13 \ C^5 + 4E + 11 \ C^4 - 4E + 09 \ C^3 + 1E + 07 \ C^2 \\ - 22137 \ C + 11.17 \ (1) \end{array}$

two methyl group C-l and C-k are appeared as a singlet at 1.65  $\delta$ ppm and 2.18  $\delta$ ppm, while the proton of C-a appeared as a doublet at 8.43–8.45  $\delta$ ppm (J = 1.2 Hz).

#### 3.3. Thermal study

Associated kinetic parameters such as order of reaction (n), activation energy ( $E_a$ ), frequency factor (A) and entropy change ( $\Delta S^*$ ) were determined according to the Freeman–Anderson method [32] using the following relation:

$$\Delta \ln dW/dt = n\Delta \ln W - (E_a/R)\Delta(1/T)$$
(8)

$$A = \left(E\beta/RT^2\right)e^{Ea/RT} \tag{9}$$

$$\Delta S^* = R \ln \left( Ah/kT \right) \tag{10}$$

Where  $\beta$  is heating rate, *R* is gas constant, *h* is Planck's constant, *T* is temperature and *k* is Boltzmann constant.

The thermal behaviour of the synthesized compound was also characterized on the basis of TGA and DTA methods. DTA and TG thermograms of  $PD_{L-H}$  are shown in Fig. 4. It is evident from Fig. 4, that  $PD_{L-H}$  is thermally stable up to about 295 °C and followed a single step degradation involving about 71.5% weight loss over the temperature range from 295 to 360 °C leaving 28.5% residue above 450 °C. The maximum weight loss was observed at about 330 °C. The characteristic temperature for the assessment of the relative thermal

stability of PD<sub>I-H</sub> was described here. Initial decomposition temperature ( $T_o$ ) of compound PD<sub>I-H</sub> was observed at 295 °C. 10% weight loss ( $T_{10}$ ) of PD<sub>I-H</sub> was observed at 310 °C. Maximum weight loss ( $T_{max}$ ) of PD<sub>I-H</sub> was observed at 330 °C and final decomposition temperature ( $T_f$ ) of PD<sub>I-H</sub> was found at 360 °C. The % weight loss of PD<sub>I-H</sub> at the end of the reaction was 28.5%. The DTA technique provides much useful information about physico-chemical changes occurring during the heating of the organic materials. DTA thermogram showed that the reaction is endothermic in nature.

The Anderson-Freeman plot is shown in Fig. 5. The determined least square values ( $R^2 = 0.987$ ) of  $E_a$  were 4918.6 kJ mol<sup>-1</sup>, n was 0.27, A was  $7.22 \times 10^{-4}$  s<sup>-1</sup> and  $\Delta S^*$  was -310.91 J K<sup>-1</sup> respectively. Degeneration process is a complex process and involves a variety of reactions taking place such as cleavage, rearrangement of crystal structure, decomposition, etc. The negative magnitude of  $\Delta S^*$  confirmed that the transition state is a much orderly state.

#### 3.4. Density, viscosity and ultrasonic velocity study

The data on the density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity (*U*) for pure solvents chloroform (CF) and *N*,*N*-dimethylformamide (DMF) at the studied temperatures were compared with the literature values and are shown in Table 1. The  $\rho$ ,  $\eta$  and *U* of pure solvents and solutions of 2-((4-acetyl-5-methyl-5-phenyl-4,5-dihydro-1,3,4-oxadiazol-2-yl)methylthio)-3-o-tolylquinazolin-4(3*H*)-one (PD<sub>I-H</sub>) in CF and DMF were determined at 303 K, 308 K and 313 K and are reported in Table 2. It is clear from Figs. 6, 7 and 8 that  $\rho$ ,  $\eta$  and *U* 

Table 4

The least-square equations and regression coefficients for PDI-H solutions in DWF at 505, 506 and 515	ns in DMF at 303, 308 and 313	-H solutions in L	coefficients for PD <sub>I</sub> .	d regression	equations and	least-square	Ine
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Parameter	Least square equations (regression coefficients, $R^2$ ) [DMF + PD <sub>I-H</sub> system]		
	303 K	308 K	313 K
$ \begin{array}{l} \rho \ (\mathrm{kg} \ \mathrm{m}^{-3}) \\ \eta \ (\mathrm{m} \ \mathrm{Pa} \ \mathrm{s}) \\ U \ (\mathrm{m} \ \mathrm{s}^{-1}) \\ Z \times 10^6 \ (\mathrm{kg} \ \mathrm{m}^{-2} \ \mathrm{s}^{-1}) \\ \kappa_a \times 10^{-10} \ (\mathrm{Pa}^{-1}) \\ L_f \times 10^{-11} \ (\mathrm{m}) \\ R_m \times 10^{-4} \ (\mathrm{m}^{10/3} \ \mathrm{s}^{-1/} \\ {}^3 \ \mathrm{mol}^{-1}) \\ b \times 10^{-5} \ (\mathrm{m}^3) \\ \pi \times 10^8 \ (\mathrm{Pa}) \end{array} $	$\begin{array}{c} 15721\ C^2-9.249\ C+942.2\ (0.984)\\ 1.256\ C+0.759\ (0.998)\\ 14428\ C^2-526.6\ C+1445.0\ (0.976)\\ 159.0\ C^2-0.512\ C+1.362\ (0.979)\\ -1078.C^2+3.604\ C+5.079\ (0.978)\\ -504.3\ C^2+1.698\ C+4.718\ (0.978)\\ 26861\ C^3-302.2\ C^2+1.582\ C+8.766\\ (0.982)\\ -119.1\ C^2+0.502\ C+7.641\ (0.964)\\ 2.468\ C+4.859\ (0.952)\\ \end{array}$	$\begin{array}{c} 26089\ C^2-65.15\ C+938.4\ (0.976)\\ 1.152\ C+0.707\ (0.982)\\ 12966\ C^2-287.1\ C+1435.0\ (0.983)\\ 159.6\ C^2-0.366\ C+1.347\ (0.982)\\ -1054\ C^2+2.260\ C+5.171\ (0.982)\\ -489.1\ C^2+1.068\ C+4.761\ (0.982)\\ 0.764\ C+8.783\ (0.986)\\ -205.4\ C^2+0.975\ C+7.672\ (0.959)\\ 2.372\ C+4.692\ (0.983)\\ \end{array}$	$\begin{array}{l} -13836\ C^2+320.8\ C+934.5\ (0.934)\\ 1.2\ C+0.635\ (0.995)\\ 847.1\ C+1402.0\ (0.978)\\ 1.014\ C+1.310\ (0.977)\\ -7.406\ C+5.44\ (0.978)\\ -3.337\ C+4.883\ (0.978)\\ -54526\ C^3+945.7\ C^2-2.663\ C+8.754\ (0.990)\\ -61608\ C^3+1134.C^2-6.684\ C+7.705\ (0.978)\\ 3.143\ C+4.63\ (0.997)\end{array}$
$V_f \times 10^{-7} (m^3)$ $S_n$	$\begin{array}{l} 307.8 \ \text{C}^2 - 5.719 \ \text{C} + 1.854 \ (0.994) \\ - 19521 \ \text{C}^3 + 3308.\text{C}^2 - 9.986 \ \text{C} + 0.021 \\ (0.975) \end{array}$	$\begin{array}{l} -1.468 \ C + 2.308 \ (0.954) \\ -7E + 06 \ C^3 - 57214 \ C^2 + 1645.C \\ -1.295 \ (0.943) \end{array}$	$\begin{array}{l} -4.154 \ C+2.316 \ (0.999) \\ 3E+11 \ C^5-4E+10 \ C^4+7E+08 \ C^3-5E+06 \ C^2 \\ +15128 \ C-9.815 \ (1) \end{array}$

increased with concentration (C) and decreased with temperature (T). The concentration and temperature dependence of these data were tested by least square analysis. Least square means that the overall solution minimizes the sum of the squares of the errors made in solving every single equation. The degree of linearity was judged on the basis of correlation coefficient. A fairly good to excellent correlation between given parameters and concentration was observed in the studied solvent systems at three temperatures. The observed correlation between  $\rho$  and C,  $\eta$  and C, and U and C is  $\gamma = 0.930 - 0.984$ , 0.982 - 0.999 and 0.929 - 0.983 respectively. The obtained  $\gamma$  values supported a fairly good to excellent linear dependence of  $\rho$ ,  $\eta$  and U with C and T. The observed trends for different *C* and *T* in  $\rho$ ,  $\eta$  and *U* were CF>DMF, DMF>CF and DMF>CF respectively (Figs. 6, 7 and 8). The increased  $\rho$ ,  $\eta$  and U with C suggest that the increase of cohesive forces is due to powerful molecular interactions, while the decrease of these parameters with T indicate that cohesive forces decreased. The increasing temperature has two opposite effects namely increase of molecular interaction (structure formation) and destruction of structure formed previously. When the thermal energy is greater than the interaction energy, it causes the destruction of previously formed structure. Thus, the increase of T favors the increase of kinetic energy and volume expansion and hence, results in the decrease of  $\rho$  and  $\eta$ . The density and viscosity of medium, pressure, temperature, etc. affect the velocity. With a view to understand the effect of concentration, temperature, nature of solvents and the structure of PD<sub>I-H</sub> on structure forming or structure-breaking tendency various acoustical parameters like adiabatic compressibility ( $\kappa_a$ ), intermolecular free path length ( $L_f$ ), Rao's molar sound function ( $R_m$ ), internal pressure ( $\pi$ ) and free volume ( $V_f$ ) were determined by using the experimental data on  $\rho$ ,  $\eta$  and U of PD<sub>I-H</sub> solutions in CF and DMF at three temperatures according to standard equations. The concentration and temperature dependence of acoustical parameters furnish a wealth of information regarding the strength of molecular interaction occurring in the solutions. Various acoustical parameters were fitted with concentration by least square analysis to certain concentration and temperature dependence molecular interactions in PD<sub>I-H</sub> solutions and hence, the structure forming or structure-breaking nature of 1,3,4-oxadiazole derivative (PD<sub>I-H</sub>) under investigation.

Ultrasonic velocity (*U*) depends on intermolecular free path length ( $L_f$ ) inversely. As can seen from Tables 3 and 4 that in CF and DMF systems both velocity and acoustical impendence (*Z*) increase with *C* and decrease with *T* of solute. The adiabatic compressibility ( $\kappa_a$ ) and intermolecular free path length ( $L_f$ ) are observed to decrease with *C* and increase with *T* suggesting the presence of solvent–solute interactions.

The decrease in  $\kappa_a$  might be due to aggregation of solvent molecules around solute molecules indicating strong solvent–solute interaction. The adiabatic compressibility ( $\kappa_a$ ) of the solutions of PD<sub>I-H</sub> was also found to decrease with *C* and increase with *T* in both systems. This phenomenon can be attributed to the solvated molecules that were fully compressed by the electrical forces of the ions. The compressibility of the solution was mainly due to the free solvent molecules. The presence of compressibility of the solution decreases with the increase in solute concentration, due to solute–solvent interactions in the system. This was further confirmed by the decrease of  $L_f$ values and the increase in viscosity of PD<sub>I-H</sub> solutions in CF and DMF.

The linear changes in  $R_m$  and b shown in Table 4 and Table 5, (correlation coefficient  $\gamma = 0.942-0.995$ ), suggest that the absence of any complex or aggregate formation takes place in both CF and DMF systems. The internal pressure ( $\pi$ ) is the resultant of forces of attraction and repulsion between the molecules in a solution. The results of adiabatic compressibility and intermolecular free path length, which were found decreased with *C* and increased with *T*, while velocity and viscosity were found increased with *C* and decreased with *T* in CF and DMF system, suggest that solute–solvent interaction is more predominant. This was confirmed from the results of internal pressure, which found increased (except at 303 K in CF). The internal pressure ( $\pi$ ) increased with *C* in both solvent systems. Internal

pressure of a solution is single factor, which plays an important role in transport properties of solutions. The internal pressure is the resultant of forces of attraction and repulsion between the molecules in solutions. The increase of internal pressure and decrease of free volume indicates an increase of cohesive forces and vice versa in the solutions of PD<sub>I-H</sub> in both solvent systems. This was further supported by free volume. Free volume  $(V_f)$  decreased with C and increased with T for solutions of PD<sub>I-H</sub> in CF and DMF (except at 303 K in CF). The increase in internal pressure and decrease in free volume with concentration in both systems indicate ordered structural arrangement due to decreasing entropy of the system. The free volume  $(V_f)$  of a solute molecule at a particular temperature and pressure depends on the internal pressure of a liquid in which it is dissolved. The decrease in free volume causes internal pressure to increase or vice versa. However, Tables 3 and 4 show that internal pressure increased and free volume decreased in CF and DMF systems. This again confirmed the existence of solute-solute and solute-solvent interactions in the system studied so far.

The degree of interaction was also measured in terms of solvation number  $(S_n)$ . The negative solvation number indicates the structurebreaking tendency of solute [33]. The decrease in the  $S_n$  with C suggested the presence of solute-solute interaction. The resultant value of the S<sub>n</sub> depends upon solvent-solute and solute-solute interactions. It is clear from Tables 3 and 4 that solvation is powerful in DMF and minimum in the CF system. The lone pairs and -Cl are electronegative groups whereas phenyl rings and -CH<sub>3</sub> are electropositive groups. Halogen group forms weak H-bond with electropositive groups and hence, solvation number was minimum in CF as compared to DMF system. It is clear from our results that S<sub>n</sub> values are positive, which shows the structure forming tendency in CF and DMF systems. The variation in Sn with C and T values was also suggesting the presence of strong dipole-dipole interaction. This is further suggestive that solutesolute and solute-solvent interactions are present in solution of PD<sub>I-H</sub> in CF and DMF.

On the basis of the experimental findings, it is concluded that  $\rho$ ,  $\eta$  and U increased with concentration and decreased with temperature in both systems. Powerful molecular interactions resulted in the structure forming as judged on the basic of positive values of solvation number. Thus, electronegative (–Cl and lone pairs) and electropositive (–CH<sub>3</sub> and phenyl rings) groups have played an important role on molecular interactions.

<sup>-1</sup>)

#### Nomenclature

С	concentration (mol $L^{-1}$ )
Т	absolute temperature (K)
М	molecular weight of solutions (kg mol
$M_1$	molecular weight of solvent
$M_2$	molecular weight of solute
$W_1$	weight fraction of solvent
$W_2$	weight fraction of solute
R	universal gas constant ( $J \mod^{-1} K^{-1}$ )
b	Van der Waals constant (m <sup>3</sup> )
m	meter
Pa	pascle
S	second

#### Greek symbol

- $\rho$  density (kg m<sup>-3</sup>)
- m viscosity (m Pa s)
- U ultrasonic velocity (m s<sup>-1</sup>)
- Z specific acoustical impedance  $(\text{kg m}^{-2}\text{s}^{-1})$
- $\kappa_a$  adiabatic compressibility (Pa<sup>-1</sup>)
- L<sub>f</sub> intermolecular free length (m)
- $R_m$  Rao's molar sound function  $(m^{10/3}s^{-1/3}mol^{-1})$
- $\pi$  internal pressure (Pa)
- $V_f$  free volume (m<sup>3</sup>)

#### Superscripts

CF	chloroform
DMF	N,N-dimethyl formamide
AR	analytical reagent

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