International Journal for Pharmaceutical Research Scholars (IJPRS)

V-1, I-2, 2012 ISSN: 2277 - 7873

RESEATCH ARTICLE

Effect of DMF on Molecular Interactions of Triazole Derivative at Different Temperatures

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Manuscript No: IJPRS/V1/I2/00023, Received On: 01/04/2012, Accepted On: 05/04/2012

ABSTRACT

The present work describes the synthesis, thermo-acoustical parameters and thermal analysis of 5-(3-methoxyphenyl)-1-phenyl-2-((m-tolylamino)methyl)-1*H*-1,2,4-triazole-3(2*H*)-thione (T4a). The viscosity (η), density (ρ) and ultrasonic sound velocity (U) of *N*,*N*-dimethyl formamide (DMF) and solutions of T4a (0.1-0.01 M) were investigated at three different temperature (303, 308 and 313) K and atmospheric pressure. Some acoustical parameters such as intermolecular free path length (L_f), adiabatic compressibility (κ_s), Rao's molar sound function (R_m), internal pressure (π), Van der Waals constant (b), free volume (V_f) and Gibbs free energy of the decomposition ($\Delta G^{\#}$), solvation number (S_n), enthalpy of activation ($\Delta H^{\#}$), pre-exponential factor (A) and entropy of activation ($\Delta S^{\#}$) were calculated. The results obtained were interpreted in terms of solute-solvent and solute-solute interactions.

KEYWORDS

Thermo-acoustical parameter, Physico-chemical study, Kinetic parameter, Molecular interaction

INTRODUCTION

Ultrasonic is a theme of broad research and as its usefulness in the fields of pharmaceuticals, engineering, biology, biochemistry, geography, polymer industry and geology is found very stimulating[1,2]. Ultrasonic has also been applied to materials characterization and process monitoring[3]. Ultrasonic sound velocity (U) together with viscosity (η) and density (ρ) provide a wealth of information about bulk properties and intermolecular forces[4,5], which found applications in several industries and technological processes. The ultrasonic sound velocity is advantageous in various field of science[6,7,8,9,10].

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The choice of 1,2,4-triazole is due to its applications in the field of medicinal chemistry. 1,2,4-Triazole signifies a group of heterocyclic compounds with a diverse of pharmaceutical and biological applications. 1,2,4-Triazole derivatives are known to exhibit antitubercular[11], antimicrobial[12], anticancer[13], anticonvulsant activities[14] and anti-inflammatory[15].

The present paper describes effect of temperature and solvent on the molecular interactions of 5-(3-methoxyphenyl)-1-phenyl-2-((m-tolylamino)methyl)-1*H*-1,2,4-triazole-3(2*H*)-thione **T4a** in *N*,*N*-dimethyl formamide (DMF) at atmospheric pressure and three different temperature (303, 308 and 313) K.

MATERIAL & METHODS

The 5-(3-methoxyphenyl)-1-phenyl-2-((m-tolylamino)methyl)-1*H*-1,2,4-triazole-3(2*H*)-thione **T4a** used in this study was synthesized

in our laboratory. The molecular weight of compound T4a is 402.15 g mole^{-1} and possible the structure of the synthesized compound T4a is shown in Figure 1.

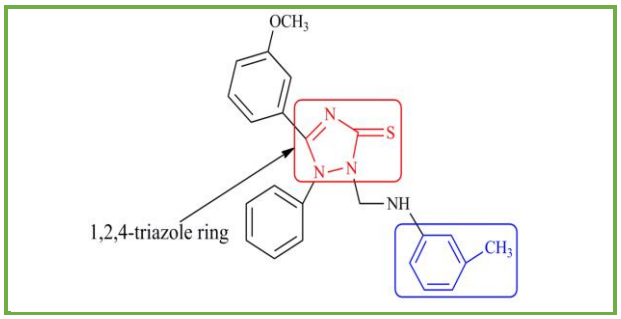

Figure 1: Structure of 5-(3-methoxyphenyl)-1-phenyl-2-((m-tolylamino)methyl)-1*H*-1,2,4-triazole-3(2*H*)-thione (T4a)

The solvent: *N*,*N*-dimethyl formamide (DMF) used in present study was of AR grade and purified according to literature method[16]. The estimated purity of solvent was more than 99.4 % and was confirmed by GC technique. The 1,2,4-triazole derivative,5-(3-methoxyphenyl)-1-phenyl-2-((m-tolylamino)methyl)-1*H*-1,2,4-triazole-3(2*H*)-thione (T4a) was synthesized according to standard protocols[17,18].

Measurements of Density, Viscosity and Ultrasonic Sound Velocity

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

Ultrasonic sound velocity of compound T4a (0.01-0.10 mol L^{-1}) in *N*,*N*-dimethyl formamide (DMF) were measured at three different temperature (303, 308 and 313) K by using F-05 multi-frequency ultrasonic interferometer (2 MHz) (Mittal Enterprise, New Delhi). Single Capillary Pycnometer made of borosil glass having knob limit of 10 mL was used to determine density. Ubbelohde viscometer with 25 mL capacity was utilized for the viscosity measurement. Ubbelohde viscometer was calibrated with fresh conductivity water immersed in a water bath that was maintained at the experimental temperature. The flow time of water (t_w) and the flow time of solution, (t_s) were measured with a digital stopwatch with an accuracy of ±0.01 s (Model: RACER HS-10W). The uncertainty of temperature is ±0.1K and that of concentration measured is ±0.001mol·dm^{-3}.

RESULT AND DISCUSSION

Density, Viscosity and Ultrasonic Sound Velocity Study

The data of the density (ρ), viscosity (η) and ultrasonic sound velocity (U) for pure solvent *N*,*N*-dimethyl formamide (DMF) at the studied temperatures were compared with the literature values and are summarized in table 1.

The ρ, η and U of pure solvent and solution of 5-(3-methoxyphenyl)-1-phenyl-2-((m-tolylamino)methyl)-1*H*-1,2,4-triazole-3(2*H*)-thione (T4a) in *N*,*N*-dimethyl formamide (DMF) were determined at (303, 308 and 313) K and are reported in table 2.

It is clear from Fig. 2 that ρ, η and U increased with concentration (C) and decreased with temperature (T). The concentration and temperature dependence of these data were tested by least square analysis.

Theoretical Equations of Acoustical Parameters

From the experimental data of density (ρ), viscosity (η) and ultrasonic sound velocity (U) various acoustical parameters like Isentropic compressibility (κ_s), Rao's molar sound function (R_m), Van der Waals constant (b), Internal pressure (π), Solvation number (S_n), Free volume (V_f), Intermolecular free path length (L_f), Viscous relaxation time (τ) were evaluated using standard equations[19,20,21,22,23].

The thermodynamic activation parameters of the decomposition process of mass loss of molecule such as entropy of activation ($\Delta S^{\#}$), pre-exponential factor (A), enthalpy of activation ($\Delta H^{\#}$) and Gibbs free energy of the decomposition ($\Delta G^{\#}$) were also calculated[24].

Least square means that the overall solution minimizes the sum of the squares of the errors made in solving every single equation.

Table 1: Comparison of measured density (ρ), viscosity (η) and ultrasonic sound velocity (U) data for pure *N*,*N*-dimethyl formamide (DMF) with literature values at (303, 308 and 313) K

Parameter0	**Experimental**			**Literature**		
Temperature	**303 K**	**308 K**	**313 K**	**303 K**	**308 K**	**313 K**
ρ (kg·m^{-3})	942.1	941.5	940.7	939.7[28]	936.8[28]	929.8[29]
η (m·Pa· s^{-1})	0.7244	0.6400	0.5417	0.7520[30]	0.7070[31]	0.6641[31]
U (m·s^{-1})	1445.60	1440.80	1406.80	1446[32]	1434.4[32]	1404[32]

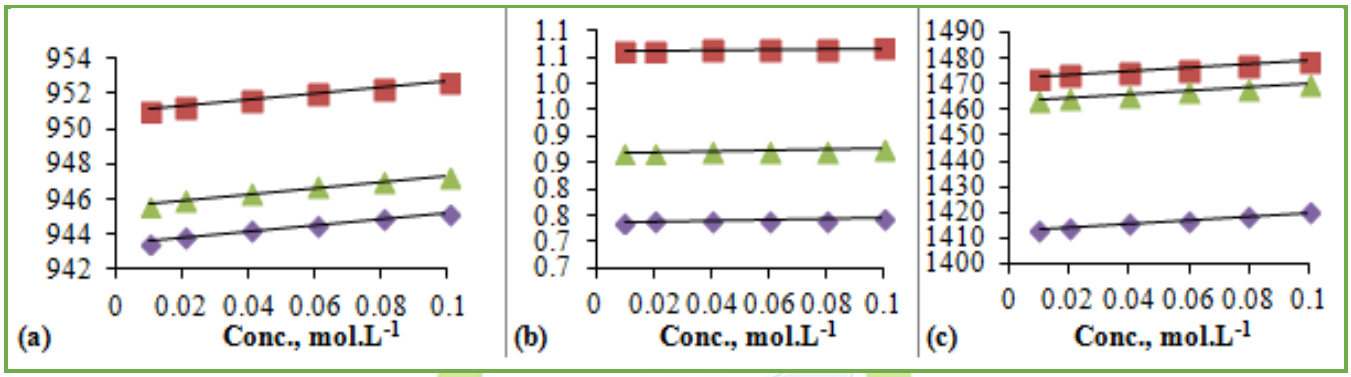

Figure 2: The plots of (a) density, (b) viscosity, and (c) sound velocity against concentration (C) for T4a in *N*,*N*-dimethyl formamide (DMF) at 303K (■), 308K (▲) and 313K (♦)

Table 2: The density (ρ), viscosity (η) and ultrasonic sound velocity (U) of compound T4a in N,N-dimethyl formamide (DMF) at (303, 308 and 313) K

Conc. (mol·L^{-1})	**Density (kg·m^{-3})**	**Viscosity (m·Pa·s)**	**Velocity (m·s^{-1})**	**Density (kg·m^{-3})**	**Viscosity (m·Pa·s)**	**Velocity (m·s^{-1})**	**Density (kg·m^{-3})**	**Viscosity (m·Pa·s)**	**Velocity (m·s^{-1})**
	303 K			**308 K**			**313 K**		
0.00	942.1	0.7244	1445.60	941.5	0.6400	1440.80	940.7	0.5417	1406.80
0.01	951.10	0.7507	1472.4	945.60	0.6643	1463.6	943.50	0.5604	1413.20
0.02	951.30	0.7516	1474.0	946.00	0.6652	1464.8	943.90	0.5613	1414.40
0.04	951.70	0.7530	1474.8	946.30	0.6662	1466.0	944.20	0.5622	1416.00
0.06	952.10	0.7541	1476.0	946.70	0.6669	1467.2	944.50	0.5630	1417.20
0.08	952.40	0.7554	1477.6	947.00	0.6678	1468.4	944.90	0.5639	1418.40
0.10	952.70	0.7564	1478.8	947.20	0.6687	1469.6	945.10	0.5647	1420.00

Table 3: The least square equations and regression coefficients of compound T4a in DMF at (303, 308 and 313) K

Parameter	**Least square equation and regression coefficient, R^2**		
	303 K	**308 K**	**313 K**
ρ, kg m^{-3}	y = 17.945x + 950.96 R^2 = 0.9953	y = 17.315x + 945.57 R^2 = 0.9736	y = 17.178x + 943.46 R^2 = 0.9783
η, m Pa s	y = 0.062x + 0.7503 R^2 = 0.9946	y = 0.0467x + 0.6641 R^2 = 0.9862	y = 0.0454x + 0.5603 R^2 = 0.9901
U, m s^{-1}	y = 67.068x + 1472.1 R^2 = 0.9829	y = 64.11x + 1463.3 R^2 = 0.9922	y = 72.11x + 1412.8 R^2 = 0.9918
Z, 10^6 kg m^{-2} s^{-1}	y = 0.0903x + 1.3999 R^2 = 0.9911	y = 0.0861x + 1.3836 R^2 = 0.9886	y = 0.0924x + 1.3329 R^2 = 0.9908
κ_s, 10^{-10} Pa^{-1}	y = -0.5294x + 4.8522 R^2 = 0.9879	y = -0.5193x + 4.939 R^2 = 0.9899	y = -0.6332x + 5.3101 R^2 = 0.9911
L_f, 10^{-11} m	y = -0.2523x + 4.6121 R^2 = 0.988	y = -0.2453x + 4.6531 R^2 = 0.99	y = -0.2886x + 4.8248 R^2 = 0.9912
R_m, 10^4 $m^{10/3}$ $s^{-1/3}$ mol^{-1}	y = 16.557x + 8.7419 R^2 = 1	y = 16.714x + 8.774 R^2 = 1	y = 16.619x + 8.6913 R^2 = 1
b, 10^{-5} m^3	y = 13.95x + 7.2359 R^2 = 1	y = 14.11x + 7.2719 R^2 = 1	y = 14.156x + 7.2725 R^2 = 1
π, 10^8 Pa	y = -8.55x + 4.7797 R^2 = 0.9979	y = -8.2298x + 4.567 R^2 = 0.9979	y = -7.8145x + 4.3318 R^2 = 0.9979
V_f, 10^{-7} m^3	y = 5.6589x + 1.9353 R^2 = 0.9999	y = 6.8237x + 2.303 R^2 = 0.9999	y = 8.3547x + 2.8198 R^2 = 0.9999
S_n	y = 251348x^4 - 42603x^3 + 1838.1x^2 + 24.598x - 0.3823 R^2 = 0.9971	y = -99135x^4 + 25845x^3 - 2250.9x^2 + 105.68x - 0.8378 R^2 = 1	y = -125859x^4 + 24238x^3 - 1583.9x^2 + 70.247x - 0.4828 R^2 = 0.9918
$\tau * 10^{13}$, s	y = -0.1335x + 4.8543 R^2 = 0.8956	y = -0.156x + 4.3734 R^2 = 0.9912	y = -0.1555x + 3.9667 R^2 = 0.9826

The degree of linearity was judged based on the correlation coefficient. A good to excellent correlation between a given parameters and concentration was observed in the studied solvent system at three temperatures. The observed correlation between ρ and C, η and C, and U and C is γ = 0.9953-0.9783, 0.9946-0.9901 and 0.9829-0.9918 respectively. The obtained γ values supported a good to excellent linear dependence of ρ, η and U with C and T.

The increase ρ, η and U with C suggest that increase of cohesive forces due to powerful molecular interactions, ultrasonic sound velocity (U) depends on intermolecular free path length (L_f) inversely. The intermolecular free path length (L_f) and isentropic compressibility (κ_s) are observed to decrease with C and increase with T suggests the presence of solvent-solute interactions. The linear changes in Rao's molar sound function (R_m) and Van der Waals constant (b) (correlation coefficient γ = 1), suggest that the absence of any complex or aggregate formation takes place in the N,N-dimethyl formamide (DMF) solvent system. The internal pressure (π) is the resultant of forces of attraction and repulsion between the molecules in a solution. Free volume (V_f) increased with C and T for solutions of **T4a** in DMF. The increase in free volume causes internal pressure to decrease or *vice versa*. The degree of interaction was also measured in terms of solvation number (S_n). It is clear from our results that S_n values are positive which shows the structure forming tendency in the N,N-dimethyl formamide (DMF) system. The value of least square equation is summarized in table 3.

The Gibbs free energy (ΔG^*), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) were also measured in N,N-dimethyl formamide (DMF) at temperatures (303, 308 and 313) K. and at atmospheric pressure. The results were extrapolated to infinite dilution, which is depicted in fig. 3. A variation in ΔG^* with C and T for compounds T4a is summarized in table 4. The value of ΔG^* for compound T4a was positive, which suggest a strong interaction between the molecules of solutes and solvent. The linear variation of ΔG^* with C also indicates that the absorption was due to rearrangement of molecules and was independent of concentration. The positive values of ΔH^* suggest that the solute–solvent interaction is endothermic in nature. The negative values of ΔS^* for the solute–solvent interaction process indicate it's not a spontaneous reaction.

CONCLUSIONS

The point of the present study is to set up the significance of solution study. The thermodynamic and acoustical behavior of 1,2,4-triazole derivative in N,N-dimethyl formamide (DMF) were evaluated at three different temperatures at atmospheric pressure and associated kinetic parameters were evaluated. Based on experimental findings, it is concluded that viscosity, density and ultrasonic sound velocity increased with concentration and decreased with temperature in the system. Powerful molecular interactions resulted in the structure forming as judged on the basis of positive values of solvation number. Thus, electropositive ($-CH_3$ and phenyl rings) groups have played an important role in molecular interactions.

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