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Thermodynamic and Acoustical study of 1-(4-Fluorophenyl)-3-(napthalen-1-yl)-2-propen-1-one

BALTHIKUMERU PADMAYYA SOWMYA

Department of Chemistry, Sri Dharmasthala Manjunatheshwara College (Autonomous), Ujire- 574240, India.
*Corresponding author E-mail: sowmyakalai@gmail.com

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ABSTRACT

The various concentrations (ranging from 0.01M to 0.1 M) of synthesized 1-(4-fluorophenyl)-3-(napthalen-1-yl)-2-propen-1-one[1] (4FNP) solutions in DMF were prepared. Density (ρ), viscosity (η) and ultrasonic velocity (U) measurements of pure solvent and solutions were carried out at 288.15 K, 293.15 K, 298.15 K and 303.15 K. The observed values of ρ, η and U were found at 298.15 K in the range of 944.50-954.25 kg.m^{-3}, 0.8440 x 10^{-3}-1.4195 x 10^{-3} Nm^{-2}s and 1454-1513 ms^{-1} respectively. The values of η and U decreased with increase of temperature, reveals the weakening of intermolecular forces between the molecules at higher temparature. Calculated thermodynamic parameters such as free volume, Gibbs free energy and internal pressures were interpreted in terms solute-solvent interaction. Increase of Gibbs free energy with increase of concentration clearly indicates the strong interaction between solvent and solute molecules. Decrease of free volume with increase in mole fraction gives evidence of strong intermolecular interaction in solution. Positive excess values of internal pressure represent the presence of dispersive forces between molecules.

Keywords: Acoustical parameters, Chalcone, Ultrasonic velocity, Gibb's free energy, Viscosity.

INTRODUCTION

Chalcones are α, β unsaturated ketones that exhibits different activities includes antimalaria[2], antitumor[3], antiviral[4], antidiabetic [5], antituberculosis[6], anticancer[7], anti-urease inhibitory[8], and others. It is found that the chalcones derived from alpha-naphthyl generally exhibit more potent anticancer activity than those of beta-naphthyl. Assessment of series of naphthalene derivatives exhibit antidepressant, anti-inflammatory and analgesic effects[1]. The studies showed that naphthalene derivatives used as a potent antimicrobial agent against different human pathogens[9]. Further, many studies revealed that fluorine substituted drug leads alter the physical properties and binding characteristics[10]. Also, fluorine substituted chalcones exhibited maximum antifungal, antibacterial and antitubercular activities[11].

The study of solute-solvent interaction plays important role in medicinal chemistry and ultrasonic interferometric measurement helps to calculate the parameters related to solute- solvent interaction[12]. Also, it gives information about complex formation and molecular association of solute in solution[13-14]. Ultrasonic parameters are directly linked with different thermodynamic quantities which help to study the interaction of solute in solution. The values of acoustical parameters as a function of concentration will be of much help in providing about the types of molecular interactions. In order to understand the kind of interaction between solute and solvent, it is of interest to calculate the acoustical parameters.

In this study density, viscosity and ultrasonic velocity measurement of 1-(fluoro)-3-(napthalen-1-yl)-2-propen-1-one (4FNP) in dimethylformamide (DMF) were carried out at 288.15 K, 293.15 K, 298.15 K and 303.15 K. The aim of carrying out this research is to study the drug suitability by studying the solute solvent interaction by viscometry and interferometric methods. The calculation of acoustical parameters in terms of concentration give information about molecular interactions in solution. Intermolecular forces between the molecules can be predicted by measuring ultrasound velocity, density and viscosity of solution of 4FNP in DMF at different temperatures.

MATERIALS AND METHODS

Synthesis of 1-(4-fluorophenyl)-3-(napthalen-1-yl)-2-propen-1-one

To a mixture of 4-fluoroacetophenone (0.01 mol) and 1-naphthaldehyde (0.01 mol) in ethanol (50 mL), 15 mL of 10% sodium hydroxide solution was added dropwise. The mixture was allowed to stand at 60°C with stirring for 6 to 8 hours. The reaction mixture was kept for overnight and acidified with glacial acetic acid. The precipitated yellow solids were collected by filtration, washed with distilled water and recrystallized from DMF. The completion of reaction was checked by TLC analysis and the products were visualized by UV detection. (Yellow solid, yield: 60% and m.p: 84-85°C)[1,15]. The reaction scheme of 4FNP is shown in Figure 1

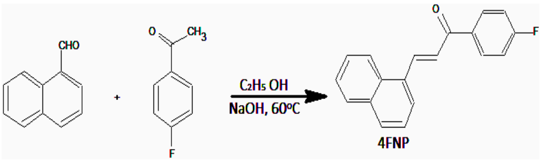

Fig. 1. Reaction scheme of synthesis of 4FNP

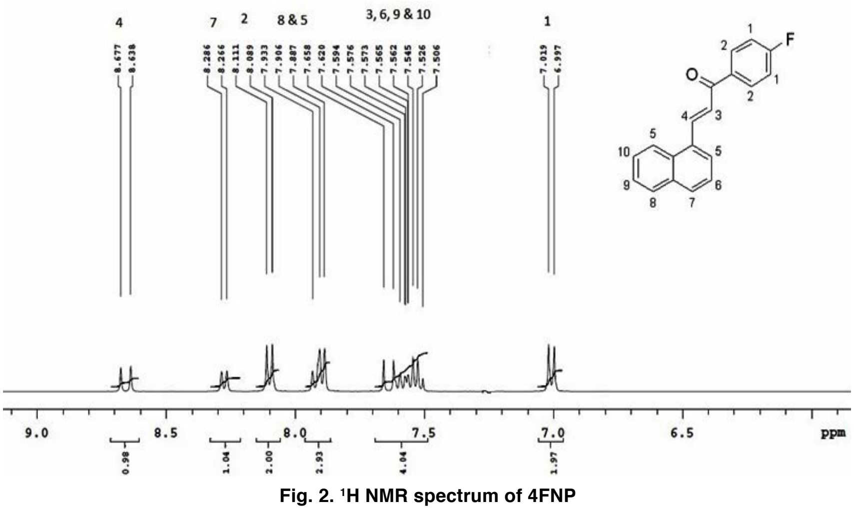

Fig. 2. ¹H NMR spectrum of 4FNP

Spectral Characterisation

^1H NMR spectrum of 4FNP was measured in $CDCl_3$ on an Agilent 400 MHz NMR spectrometer is shown in Figure 2.

^{1}H NMR (400 MHz, $CDCl_3$, delta, ppm): 6.997-7.019 (2H, d, H-1, J=8.8 Hz), 7.506-7.594 (4H, m, H-3, H-6, H-9 & H-10), 7.887-7.906 (3H, d, H-8 & H-5, J=7.6 Hz), 8.089-8.111 (2H, d, H-2, J=8.8 Hz), 8.266-8.286 (1H, d, H-7, J=8 Hz), 8.638-8.677 (2H, d, H-4, J=15.6Hz)

Study of Acoustical Parameters[16]

Single crystal interferometer has been used for the measurement of ultrasonic velocities. Pycnometer and Ubbelohde viscometer have been used for the measurement of density and viscosity respectively. Using the data obtained from the experiment, various acoustical parameters are calculated in different solutions. The purified and AR grade DMF used as a solvent in present work. The calculations of acoustical properties require the measurements of ultrasonic velocity (U), viscosity (η) and density (ρ).

Density Measurements

The weight of distilled water, DMF and different concentrated solutions of 4FNP in DMF were measured at 288.15 K, 293.15 K, 298.15 K and 303.15 K by using pycnometer. The density (ρ) of different concentrated solutions were determined by using following equation (1)

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

Where w & w_0 are weight of solution & water respectively and ρ_o is the density of water[17].

Viscosity Measurements

10 mL of the test solution was pipetted and introduced to the Ubbelohde viscometer. The Ubbelohde viscometer was suspended in a viscometer bath at specific temperature. The time of flow for DMF and different concentrated solution of 4FNP were measured at 288.15 K, 293.15 K, 298.15 K and 303.15 K. The viscosity of solutions was determined using equation (2).

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

Where t, t_o and η_o are the flow time of solution, time of solvent and viscosity of DMF[18] respectively.

Sound Velocity Measurement

Sound velocity of test solution was determined using Ultrasonic interferometer. Mittal Ultrasonic interferometer of Model No. F-81 was used for the study. The measuring cell consists of quartz crystal and micrometre was filled with 2 mL of solvent/solution. The temperature of DMF/ different concentrated solution of 4FNP in the cell was maintained by water circulation from the thermostat. Maximum/minimum of anode current (n) was obtained by slow rotation of micrometre. The wave length (λ) and sound velocity (U) were calculated using the equations (3) & (4).

$$\lambda = \frac{2d}{n} \qquad (3)$$

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

where, F = 3 x 10^6 Hertz.

The following thermodynamic parameters are calculated by using following standard expressions[19]

1. Isentropic compressibility[20] (β):

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

2. Intermolecular free path length[20] (L_f):

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

Where K_J = 2.0965 X 10^{-6} is known as Jacobson constant

3. Acoustic impedance (Z):

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

4. Relaxation Strength (r):

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

Where U_∞ = 1.6 x 10^5 cm.s^{-1}

5. Molar compressibility (W):

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

The apparent molecular weight (M) of the solution can be calculated as[16]:

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

6. Apparent molar volume (ϕ_V)

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

7. Apparent molar compressibility (ϕ_β)

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

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

8. Solvation number (S_n)

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

9. Free Volume (V_f)

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

10. Internal Pressure (π)

$$\pi = \frac{P_f R T \rho^{2/3}\left[\frac{K\eta}{U}\right]}{M^{7/6}} \tag{15}$$

Where P_f is the packing factor (= 2), η is viscosity of solution and K is a constant ($K = 4.28 \times 10^9$)

11. Gibb's Free Energy (ΔG)

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

Where τ is the viscous relaxation time.

RESULTS AND DISCUSSION

The density (ρ), viscosity (η) and sound velocity (U) of pure DMF and solutions of 4FNP in DMF were determined experimentally at 288.15 K, 293.15 K, 298.15 K and 303.15 K and are given in Table 1. It is observed that ultrasound velocity, density and viscosity were decreases when the temperature increased and also ultrasound velocity, density and viscosity were increases with increase of concentrations of solution and are shown in Fig. 3 & 4. Decrease of Ultrasound velocity and viscosity with increase of temperature reveals the weakening of intermolecular forces between the molecules. So molecular interaction between the molecules decreases.

Different acoustical parameters were calculated from these experimental data using equations (1) to (16) at 288.15 K, 293.15 K, 298.15 K and 303.15 K. The calculated acoustical parameters are given in Table 2 and shown in Fig. 5- Figure 10.

The variation of isentropic compressibility (β) and the intermolecular free length (L_f) with concentration in DMF at different temperatures are shown in Fig. 5 and Fig. 6. It depicts that both isentropic compressibility (β) and the intermolecular free length (L_f) decreases continuously with increase of concentration of solutions and the same increases with rise in temperature. The decrease of L_f indicates that there is strong interaction between solvent and solute molecules. Fig. 7 shows variation of molar compressibility (W) with concentration at different temperatures. The increase of W with concentration indicates that there is an increase of molecular interaction. Free volume (V_f) decreases with increase in mole fraction indicates intermolecular interaction seems to be stronger than the intramolecular interaction shown in Fig. 8. Variation of Internal Pressure (π) and Gibbs free energy (ΔG) with increase of concentration at different temperatures are shown in Fig. 9 and Fig. 10. 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 1: The density (ρ), ultrasonic velocity (U) and viscosity (η) of 4FNP in DMF at 288.15, 293.15, 298.15 K and 303.15 K

Conc. (M)	ρ (kg.m^{-3})	U (m.s^{-1})	$\eta \times 10^{-3}$ (Nm^{-2}s)	Conc. (M)	ρ (kg.m^{-3})	U (m.s^{-1})	$\eta \times 10^{-3}$ (Nm^{-2}s)
T= 288.15 K				T= 293.15 K			
0.00	954.20	1478	0.940	0.00	949.40	1460	0.8920
0.01	955.53	1491	1.0087	0.01	950.42	1473	0.9564
0.02	957.85	1504	1.0941	0.02	952.74	1489	1.0331
0.04	959.36	1517	1.2288	0.04	954.25	1503	1.1501
0.06	960.91	1529	1.3652	0.06	955.82	1515	1.2592
0.08	962.21	1539	1.4992	0.08	957.21	1527	1.3816
0.10	964.12	1551	1.6311	0.10	959.23	1539	1.5186
T= 298.15 K				T= 303.15 K			
0.00	944.50	1454	0.8440	0.00	939.80	1447	0.8090
0.01	946.32	1462	0.8811	0.01	940.19	1454	0.8409
0.02	947.62	1471	0.9475	0.02	942.49	1461	0.9220
0.04	949.16	1482	1.0676	0.04	944.01	1470	1.0161
0.06	950.71	1493	1.1822	0.06	945.56	1482	1.1044
0.08	952.25	1505	1.3032	0.08	947.08	1495	1.1954
0.10	954.25	1513	1.4192	0.10	949.14	1507	1.2911

Table 2: Various Acoustical parameters of 4FNP at 298.15 K

Conc. (M)	$\beta \times 10^{-10}$ m^2N^{-1}	$L_f \times 10^{-11}$(m)	$Z \times 10^{-6}$ (Nm^{-2})	r	$W \times 10^{-3}$	$V_f \times 10^{-3}$ (m^3mol^{-1})	$\pi \times 10^3$ (atm)	$\Delta G \times 10^{-21}$ ($kJmol^{-1}$)	ϕ_V(m^3mol^{-1})	ϕ_β(m^2N^{-1})	S_n
T= 288.15 K											
0.00	4.7975	4.5920	1.4103	0.1467	7.4239	4.3918	1.6799	0.5420	-	-	-
0.01	4.7076	4.5488	1.4247	0.1316	7.4506	4.0198	1.7285	0.5633	3.3886	-64.3037	-37.5194
0.02	4.6154	4.5040	1.4406	0.1164	7.4700	3.6200	1.7896	0.5886	3.3722	-23.2423	-13.5612
0.04	4.5295	4.4619	1.4553	0.1011	7.4751	3.1065	1.8782	0.6286	3.3616	-7.8314	-4.5694
0.06	4.4515	4.4233	1.4692	0.0868	7.4815	2.7065	1.9615	0.6648	3.3507	-0.8141	-0.4750
0.08	4.3879	4.3916	1.4808	0.0748	7.4818	2.3943	2.0378	0.6974	3.3417	0.8880	0.5181
0.10	4.3117	4.3533	1.4954	0.0603	7.4907	2.1519	2.1068	0.7249	3.3285	1.9411	1.1326
T= 293.15 K											
0.00	4.9413	4.6603	0.1673	1.3861	7.3926	4.6645	1.6409	0.5326	-	-	-
0.01	4.8493	4.6167	0.1524	1.4000	7.4191	4.2755	1.6873	0.5536	3.4251	-63.8108	-37.0446
0.02	4.7341	4.5616	0.1339	1.4186	7.4430	3.8865	1.7415	0.5754	3.4084	-23.0394	-13.3752
0.04	4.6390	4.5155	0.1176	1.4342	7.4496	3.3834	1.8190	0.6112	3.3977	-7.7457	-4.4967
0.06	4.5583	4.4760	0.1034	1.4481	7.4562	3.0136	1.8858	0.6413	3.3865	-0.7786	-0.4520
0.08	4.4804	4.4376	0.0892	1.4617	7.4595	2.6750	1.9570	0.6723	3.3767	0.9028	0.5241
0.10	4.4015	4.3984	0.0748	1.4763	7.4687	2.3677	2.0339	0.7039	3.3625	1.9422	1.1275
T= 298.15 K											
0.00	5.0081	4.6917	0.1742	1.3733	7.3784	5.0368	1.5940	0.5040	-	-	-
0.01	4.9439	4.6615	0.1651	1.3835	7.3987	4.7810	1.6209	0.5158	3.4549	-63.8965	-36.9028
0.02	4.8769	4.6298	0.1547	1.3940	7.4114	4.3454	1.6718	0.5487	3.4454	-22.8585	-13.2017
0.04	4.7969	4.5917	0.1421	1.4067	7.4141	3.7041	1.7587	0.5829	3.4342	-7.6756	-4.4330
0.06	4.7188	4.5542	0.1293	1.4194	7.4194	3.2406	1.8341	0.6099	3.4230	-0.7499	-0.4331
0.08	4.6363	4.5142	0.1152	1.4331	7.4232	2.8571	1.9079	0.6346	3.4119	0.9083	0.5246
0.10	4.5778	4.4857	0.1058	1.4438	7.4269	2.5545	1.9762	0.6588	3.3977	1.9428	1.1220
T= 303.15 K											
0.00	5.0819	4.7262	0.1821	1.3599	7.3630	5.3284	1.5591	0.4865	-	-	-
0.01	5.0310	4.7024	0.1742	1.3670	7.3802	5.0860	1.5810	0.4951	3.5000	-62.8200	-36.1005
0.02	4.9708	4.6742	0.1662	1.3770	7.3913	4.4804	1.6489	0.5248	3.4830	-22.6258	-13.0023
0.04	4.9022	4.6418	0.1559	1.3877	7.3911	3.9411	1.7164	0.5571	3.4718	-7.5716	-4.3512
0.06	4.8152	4.6005	0.1421	1.4013	7.3980	3.5496	1.7728	0.5842	3.4604	-0.7007	-0.4027
0.08	4.7242	4.5568	0.1269	1.4159	7.4033	3.2197	1.8268	0.6107	3.4493	0.9410	0.5408
0.10	4.6392	4.5156	0.1129	1.4304	7.4128	2.9265	1.8819	0.6351	3.4344	1.9607	1.1268

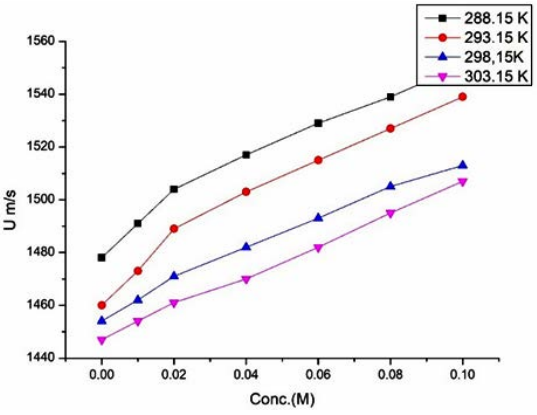

Fig. 3. Plot of Ultrasonic velocity vs Concentration of 4FNP in DMF at 288.15, 293.15, 298.15 K and 303.15 K

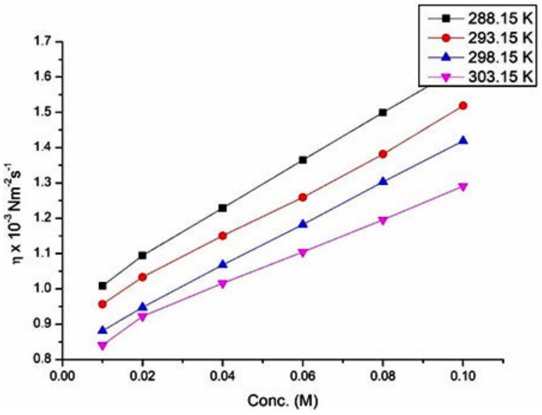

Fig. 4. Plot of Viscosity vs Concentration of 4FNP in DMF at 288.15, 293.15, 298.15 K and 303.15 K

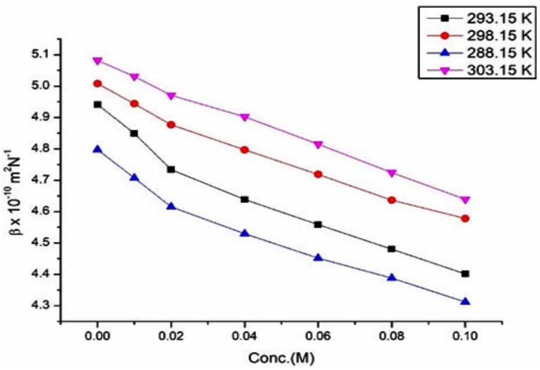

Fig. 5. Plot of Isentropic compressibility vs Concentration of 4FNP in DMF at 288.15, 293.15, 298.15 K and 303.15 K

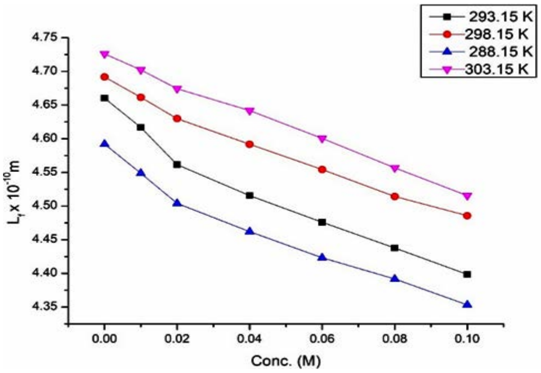

Fig. 6. Plot of intermolecular free length (L_f) vs Concentration of 4FNP in DMF at 288.15, 293.15, 298.15 K and 303.15 K

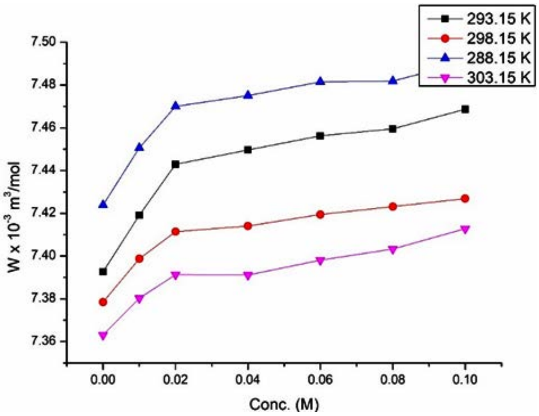

Fig. 7. Plot of Molar compressibility (W) vs Concentration of 4FNP in DMF at 288.15, 293.15, 298.15 K and 303.15 K

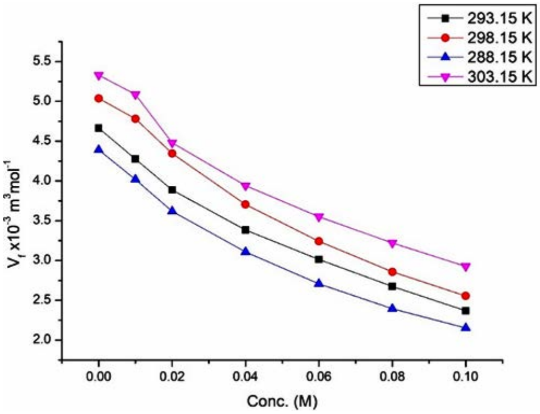

Fig.8. Plot of Free volume (V_f) vs Concentration of 4FNP in DMF at 288.15, 293.15, 298.15 K and 303.15 K

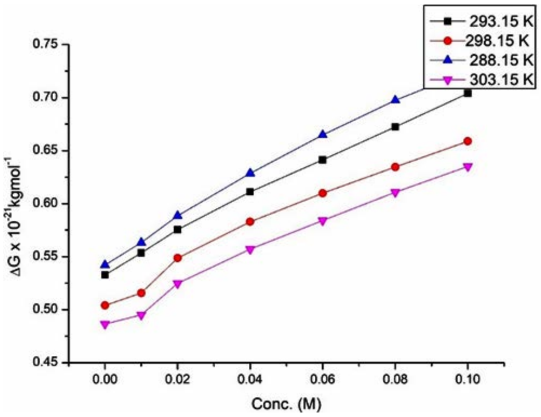

Fig. 9. Plot of Gibbs free energy (ΔG) vs Concentration of 4FNP in DMF at 288.15, 293.15, 298.15 K and 303.15 K

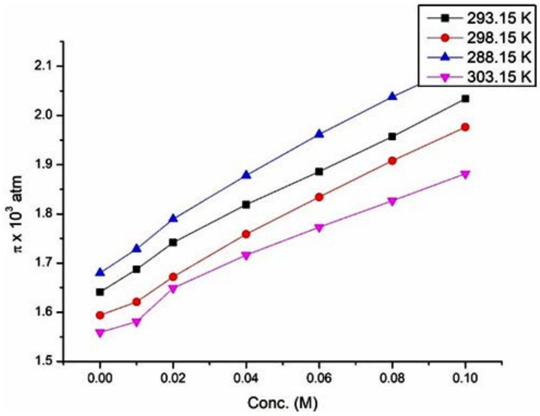

Fig. 10. Plot of Internal Pressure (π) vs Concentration of 4FNP in DMF at 288.15, 293.15, 298.15 K and 303.15 K

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Conflict of interest

The author declare that we have no conflict of interest.

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