



Effect of temperature on thermo-physical properties of pyrazolo quinazoline derivatives by ultrasonic studies

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ABSTRACT

Density (ρ), Sound velocity (U) and viscosity (η) of pure solvent N,N-dimethylformamide (DMF) and solutions of pyrazolo quinazoline derivatives in DMF were taken at different concentration range and at different temperatures by using Antone paar. From these experimental data, some acoustical parameters such as adiabatic compressibility (κ_s), intermolecular free length (L_f), solvation number (S_n), apparent molar compressibility (ϕ_k), apparent molar volume (ϕ_v), internal pressure (π) etc., have been determined and correlated with the concentration (C). With concentration and temperatures, Linear or non-linear increases or decreases of acoustical parameters shows the existence of strong molecular interactions between solute and solvent. The results are interpreted in terms of solute-solute and solute-solvent interactions to understand the behavior of synthesized compounds in solutions.

Keywords: pyrazolo quinazoline derivatives; Acoustical parameter; Molecular interactions; Density; apparent molar compressibility

1. INTRODUCTION

The study of pyrazolo quinazoline derivatives has been revealed valuable drugs for various diseases. Quinazoline derivatives are of much interest of organic chemistry from a long time because of their wide pharmacological activities [1-10]. So, many pyrazolo quinazoline derivatives have been synthesized because of their application in pharmaceutical industries [11-14]. Owing to their applications, it would be interesting to study the molecular interactions of solutions of these compounds which may be helpful for biochemists and microbiologists to understand the mechanism of transport of these compounds through membranes or tissues.

Ultrasonic velocity measurement is one of the best tools to understand the nature of molecular interactions and investigating the physicochemical behavior occurring in the solution [15]. Ultrasonic and thermodynamic studies of molecular interactions have significant importance in industry and engineering field [16]. Further, ultrasonic velocity measurements have been much useful in understanding the molecular interactions in liquid mixtures. Ultrasonic velocity [17] and viscosity [18] have been widely used in the field of interactions and structural evaluation process. The relaxation studies of polar molecules in polar solvents have been widely used to study the molecular structures including the molecular interactions in liquid mixtures [19,20]. Many types of molecular interactions that may operate between molecules of different types are dispersion forces, hydrogen bonding and dipole and dipole-induced dipole interactions.

In the present study, pyrazolo quinazoline derivatives have been synthesized and their structures are confirmed by IR, NMR and Mass spectral data. The density, sound velocity and viscosity of synthesized compounds are measured in N,N-dimethylformamide solutions of wide range of concentrations different temperatures (298.15 K, 308.15 K, and 318.15 K). With these experimental data, some acoustical parameters such as adiabatic compressibility (κ_s), intermolecular free length (L_f), solvation number (S_n), apparent molar compressibility (ϕ_c), apparent molar volume (ϕ_v) etc., have been computed to shed more light on such interactions.

2. EXPERIMENTAL

Materials:

The DMF used was of AR grade supplied by Spectrochem Pvt. Ltd. (Mumbai, India) and was purified according to the standard procedure [21]. The distilled DMF was stored over molecular sieves. The purity of DMF was confirmed by GC-MS (SHIMADZU-Model No.-QP-2010) equipped with column (DB-5MS, 25 m in length, 0.20 mm internal diameter and 0.33 μm film) and was found to be 99.99%.

Synthesis:

The detailed synthesis of pyrazolo quinazolines are reported earlier [22] and the reaction scheme is shown in Figure 1.

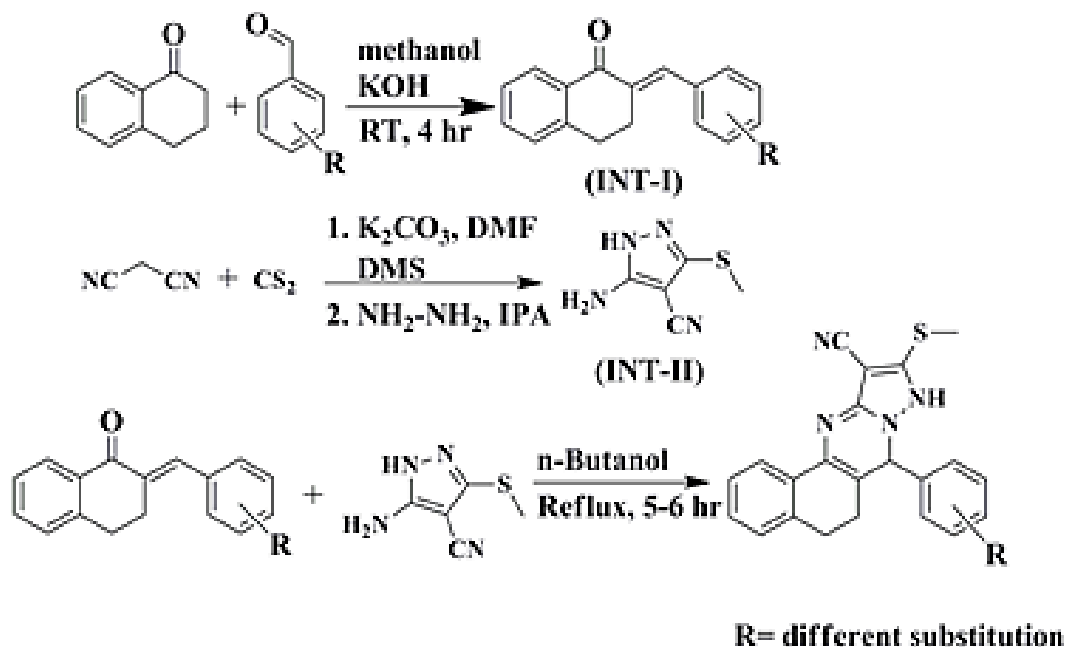


Figure 1. Synthesis scheme of pyrazolo quinazoline derivatives.

Spectroscopy study:

The characterization of all these compounds was done by IR, NMR and mass spectral data. The IR spectra were recorded on IR affinity 1S (furrier transport infra-red spectroscopy). The Mass spectra were recorded on Shimadzu GC-MS-QP-2010 model using direct inlet probe technique. ^1H NMR was determined in DMSO solution on a Bruker Ac 400 MHz spectrometer. Elemental analysis was done by Elemental analyser EURO EA 3000 instrument. The physical constants of all the five synthesized compounds (K-1 to K-5) are given in Table 1.

Table 1. Physical properties of synthesized pyrazolo quinazoline derivatives.

<i>Compound Code</i>	<i>Substitution R</i>	<i>Molecular Formula</i>	<i>Molecular Weight</i>	<i>Yield (%)</i>
K-1	-4-CN	$\text{C}_{23}\text{H}_{17}\text{N}_5\text{S}$	395.12	75
K-2	-3-Cl	$\text{C}_{22}\text{H}_{17}\text{ClN}_4\text{S}$	404.09	72
K-3	-3-OCH ₃	$\text{C}_{23}\text{H}_{20}\text{N}_4\text{OS}$	400.14	79
K-4	-3-Br	$\text{C}_{22}\text{H}_{17}\text{BrN}_4\text{S}$	448.04	71
K-5	-4-CH ₃	$\text{C}_{23}\text{H}_{20}\text{N}_4\text{S}$	384.14	69

Measurements of Density, Viscosity and Ultrasound Velocity:

Apparatus and procedure:

Solutions of different concentrations were made in DMF of all the synthesized compounds.

Measurements of Density, and Ultrasound velocity:

The ultrasonic velocity and density measurements of pure solvent DMF and solutions of different pyrazolo quinazoline derivatives have been done by using Antone Paar Density and Sound Velocity meter (DSC 5000M) with accuracy of density and velocity are $\pm 0.005 \text{ kg/m}^3$ and $\pm 0.5 \text{ m/s}$ respectively. The instrument was fully automated and the temperature was automatically controlled. Calibration was carried out using double distilled water.

Measurement of viscosity:

The Ubbelohde viscometer with 25 ml capacity was used for the viscosity measurement with accuracy $\pm 0.06\%$. The 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 stop watch with an accuracy of $\pm 0.01 \text{ s}$ (Model: RACER HS-10W). The flow time of water is 28.22 sec, 24.22 sec and 21.40 sec at 298.15 K, 308.15 K and 318.15 K respectively. The temperature stability was maintained by circulating water from a thermostat (NOVA NV-8550 E, accuracy of $\pm 0.1 \text{ K}$) around the viscometer. The accuracy of viscosity is $\pm 0.05 \%$

3. RESULTS AND DISCUSSION

The physical properties of all the synthesized compounds are given in Table 1 with their side chain substitution. Figures 2 and 3 show IR and ^1H NMR spectrum for the compound K-1 respectively

Spectral Data:

K-1:

IR (cm^{-1} , KBr): 3475.85 (-NH (sec.) str.), 3049.56 (Ar-H str.), 2924.18 (-CH₂ sym. str.), 2227.86 (-CN str.), 1664.62 (C=C str. α , β unsaturated 6-member ring), 1604.83 (-NH bending vib. Secondary amine), 1381.08 (-CH bending.), 1315.50 (C-N (sec) bending.), 1242-1010 (C-H in plane bending, phenyl ring), 767.69 (C-H str. 5-adjacent c atoms), **^1H NMR (DMSO-*d*₆) δ (ppm):** 2.389 (3H, singlet, -CH₃), 1.713-2.796 (4H, multiplet, C-H), 6.170 (1H, singlet, C-H), 7.196-7.936 (8H, multiplet C-H), 10.201 (1H, singlet, -NH), **MS: (*m/z*) = 395**

K-2:

IR (cm^{-1} , KBr): 3284.83 (-NH (sec.) str.), 3064.99 (Ar-H str.), 2908.75 (-CH₂ sym. str.), 2225.93 (-CN str.), 1666.55 (C=C str. α , β unsaturated 6-member ring), 1604.83 (-NH bending vib. Secondary amine), 1383.01 (-CH bending.), 1336.71 (C-N (sec) bending.), 1242-1010 (C-H in plane bending, phenyl ring), 767.69 (C-H str. 5-adjacent c atoms), 731.05 (C-H in plane

bending), $^1\text{H NMR (DMSO-}d_6)$ $\delta(\text{ppm})$: 2.400 (3H, singlet, -CH₃), 1.785-2.750 (4H, multiplet, C-H), 6.068 (1H, singlet, C-H), 7.216-7.704 (8H, multiplet C-H), 10.139 (1H, singlet, -NH). **MS**: (m/z) = 404

K-3:

IR (cm⁻¹, KBr): 3479.70 (-NH (sec.) str.), 3037.99 (Ar-H str.), 2918.40 (-CH₂ sym. str.), 2227.86 (-CN str.), 1666.55 (C=C str. α,β unsaturated 6-member ring), 1599.04 (-NH bending vib. Secondary amine), 1381.08 (-CH bending.), 1319.08 (C-N (sec) bending.), 1242-1010 (C-H in plane bending, phenyl ring), 1093.67 (C-F str.), 725.26 (C-H str. 5-adjacent c atoms), $^1\text{H NMR (DMSO-}d_6)$ $\delta(\text{ppm})$: 2.428 (3H, singlet, -CH₃), 3.687 (3H, singlet-OCH₃), 1.799-2.787 (4H, multiplet, C-H), 6.007 (1H, singlet, C-H), 7.198-7.697 (8H, multiplet C-H), 10.125 (1H, singlet, -NH). (4.00). **MS**: (m/z) = 400

K-4:

IR (cm⁻¹, KBr): 3257.88 (-NH (sec.) str.), 3047.63 (Ar-H str.), 2929.97 (-CH₂ sym. str.), 2227.86 (-CN str.), 1653.05 (C=C str. α,β unsaturated 6-member ring), 1604.83 (-NH bending vib. Secondary amine), 1383.01 (-CH bending.), 1315.50 (C-N (sec) bending.), 1242-1010 (C-H in plane bending, phenyl ring), 723.33 (C-H str. 5-adjacent c atoms), 582.52 (C-Br str.), $^1\text{H NMR (DMSO-}d_6)$ $\delta(\text{ppm})$: 2.397 (3H, singlet, -CH₃), 1.742-2.795 (4H, multiplet, C-H), 6.057 (1H, singlet, C-H), 7.202-7.740 (8H, multiplet C-H), 10.123 (1H, singlet, -NH). **MS**: (m/z) = 448

K-5:

IR (cm⁻¹, KBr): 3236.66 (-NH (sec.) str.), 3007.12 (Ar-H str.), 2929.97 (-CH₂ sym. str.), 2224.40 (-CN str.), 1666.55 (C=C str. α, β unsaturated 6-member ring), 1604.83 (-NH bending vib. Secondary amine), 1383.09 (-CH bending), 1334.78 (C-N (sec) bending.), 1242-1010 (C-H in plane bending, phenyl ring), 702.11 (C-H str. 5-adjacent c atoms), 731.05 (C-H in plane bending), $^1\text{H NMR (DMSO-}d_6)$ $\delta(\text{ppm})$: 2.442 (3H, singlet, -CH₃), 3.023 (3H, singlet -CH₃), 1.788-2.769 (4H, multiplet, C-H), 6.005 (1H, singlet, C-H), 7.102-7.767 (8H, multiplet C-H), 10.189 (1H, singlet, -NH), **MS**: (m/z) = 384

$^1\text{H-NMR spectra}$:

The $^1\text{H NMR}$ spectra of compound K-1 is shown in Figure 3. The residual peak of DMSO is shown as a singlet at 3.366 δppm . The peak of S-CH₃ is shown around 2.389 δppm . The protons of cyclo hexane ring are shown in aliphatic region at the range 1.713-2.796 δppm . Chiral proton is clearly shown at 6.170 δppm which is proof of ring cyclization. The aromatic protons of two phenyl rings are shown in the aromatic range between 7.196-7.936 δppm with their appropriate multiplicity. At the range of 7.448-7.857, double doublet is clearly shown which is confirmation of attachment of -CN group at p-position. One proton is at 10.201 δppm as singlet gives confirmation of pyrazole ring. Due to attachment of one proton with nitrogen, this is shown at highly deshielded region.

Density, viscosity and ultrasonic velocity study:

Table 2 shows the density (ρ), viscosity (η) and ultrasonic velocity (U) values of pure solvent DMF along with their literature values. It is observed that there is good agreement

between experimental and literature values. The experimental data of density, ultrasonic velocity and viscosity for the compounds in DMF solutions at different temperatures are given in Table 3. It is clearly shown from Table 3 that by increasing concentration, density, ultrasonic velocity and viscosity increases. More visually, the variation of ultrasonic velocity with concentrations is given in Figure 4 at different temperatures for studied compounds.

Table 2. Density, Viscosity and Ultrasonic velocity of pure solvents at pyrazolo quinazoline derivatives

<i>Solvent</i>	<i>Temp.</i>	ρ Kg/m ³		η mPa.s		<i>U</i> m/s	
		This work	Ref.	This work	Ref.	This work	Ref.
<i>DMF</i>	298.15 K	943.94	943.90[21]	0.8158	0.8040[37]	1457.71	1457.49[36]
			943.94[36]				
	308.15 K	934.38	934.60[44]	0.7011	0.7103[36]	1418.80	1418.95[36]
			934.64[42]				
	318.15 K	924.77	925.80[38]	0.6337	0.6348[36]	1380.15	1379.60[39]

Table 3. The density (ρ), ultrasonic velocity (*U*) and viscosity (η) of pyrazolo quinazoline derivatives in DMF at different temperatures.

<i>Concentration (M)</i>	<i>Density Kg/m³</i>	<i>Velocity m/s</i>	<i>Viscosity Nsm⁻²</i>	<i>Density Kg/m³</i>	<i>Velocity m/s</i>	<i>Viscosity Nsm⁻²</i>
298.15 K						
K-1			K-2			
0.0	943.94	1457.71	0.8158	943.94	1457.71	0.8158
0.01	945.48	1462.18	0.8358	945.13	1462.87	0.8310
0.02	946.83	1463.68	0.8469	947.61	1464.87	0.8401
0.04	949.33	1466.13	0.8642	949.31	1467.99	0.8663
0.06	951.46	1467.56	0.8810	951.53	1470.68	0.8928
0.08	953.03	1468.91	0.9018	952.75	1473.59	0.9112
0.10	954.17	1470.67	0.9129	953.15	1477.36	0.9349
K-3			K-4			
0.00	943.94	1457.71	0.8158	943.94	1457.71	0.8158
0.01	946.88	1462.32	0.8406	946.698	1462.78	0.8420
0.02	947.90	1464.51	0.8542	948.517	1466.39	0.8680
0.04	948.97	1467.21	0.8943	952.393	1469.98	0.8927
0.06	950.19	1469.99	0.9070	956.006	1472.45	0.9329
0.08	952.28	1470.93	0.9404	959.262	1474.87	0.9528

0.10	952.63	1473.63	0.9674	959.71	1479.15	0.9752
K-5						
0.00	943.94	1457.71	0.8158			
0.01	945.70	1461.89	0.8372			
0.02	946.90	1463.79	0.8533			
0.04	948.92	1466.51	0.8705			
0.06	949.34	1469.54	0.8823			
0.08	951.00	1471.82	0.9014			
0.10	951.70	1474.93	0.9244			

308.15 K

	K-1			K-2		
0.00	934.38	1418.80	0.7011	934.38	1418.80	0.7011
0.01	936.43	1424.59	0.7305	936.28	1424.17	0.7295
0.02	937.68	1425.74	0.7408	937.16	1427.17	0.7437
0.04	940.19	1427.72	0.7602	939.54	1429.99	0.7631
0.06	942.32	1428.76	0.7758	942.65	1432.34	0.7866
0.08	944.30	1430.28	0.7947	944.16	1435.06	0.8085
0.10	945.43	1432.14	0.8141	946.26	1437.58	0.8271

	K-3			K-4		
0.00	934.38	1418.80	0.7011	934.38	1418.80	0.7011
0.01	936.03	1424.12	0.7302	937.15	1424.45	0.7372
0.02	937.11	1426.72	0.7558	938.96	1428.54	0.7615
0.04	939.03	1429.15	0.7855	942.84	1431.95	0.7893
0.06	941.17	1431.69	0.8006	946.44	1435.48	0.8088
0.08	943.46	1432.74	0.8345	949.61	1438.03	0.8334
0.10	945.11	1434.32	0.8559	950.02	1442.17	0.8580

	K-5		
0.00	934.38	1418.80	0.7011
0.01	935.23	1424.09	0.7290
0.02	936.48	1426.04	0.7395
0.04	938.94	1428.71	0.7601
0.06	940.12	1431.33	0.7768
0.08	941.85	1433.95	0.7944
0.10	943.03	1436.46	0.8169

318.15 K

	K-1			K-2		
0.00	924.77	1380.15	0.6337	924.77	1380.15	0.6337
0.01	926.43	1386.76	0.6484	926.33	1386.15	0.6483
0.02	927.69	1388.19	0.6587	927.97	1389.17	0.6620
0.04	930.20	1390.16	0.6707	930.24	1392.57	0.6822
0.06	932.33	1391.75	0.6895	932.14	1395.67	0.7054
0.08	933.90	1393.45	0.7033	934.22	1398.69	0.7222
0.10	935.55	1395.16	0.7172	936.74	1401.27	0.7413

K-3				K-4		
0.00	924.77	1380.15	0.6337	924.77	1380.15	0.6337
0.01	928.13	1386.18	0.6556	927.54	1386.98	0.6523
0.02	928.81	1387.86	0.6767	929.35	1391.55	0.6709
0.04	929.89	1391.35	0.6932	933.23	1395.24	0.6902
0.06	930.98	1394.17	0.7082	937.22	1397.89	0.7158
0.08	933.08	1395.45	0.7342	940.39	1400.88	0.7344
0.10	934.56	1397.64	0.7506	941.53	1403.75	0.7567
K-5						
0.00	924.77	1380.15	0.6337			
0.01	926.13	1386.06	0.6503			
0.02	926.99	1387.89	0.6663			
0.04	928.80	1391.26	0.6804			
0.06	929.93	1394.05	0.6993			
0.08	931.60	1396.88	0.7202			
0.10	932.45	1399.47	0.7392			

To study molecular interactions of compounds in solutions, some acoustical and apparent parameters such as acoustical impedance (Z), intermolecular free length (L_f), adiabatic compressibility (κ_s), internal pressure (π), solvation number (S_n), apparent molar compressibility (ϕ_k), apparent molar volume (ϕ_v) etc., have been evaluated using experimental data of ultrasonic velocity (U), density (ρ) and viscosity (η) by following equations.

Specific acoustical impedance: $Z = U\rho$ (1)

Intermolecular free path length [23]: $L_f = K_j \kappa_s^{1/2}$ (2)

Adiabatic compressibility [24, 25]: $\kappa_s = \frac{1}{U^2 \rho}$ (3)

Internal pressure [26]: $\pi = bRT \left[\frac{K_\eta}{U} \right]^{1/2} \frac{\rho^{2/3}}{M^{7/6}}$ (4)

Vander Waals constant:

$$b = \frac{M}{\rho} \left\{ 1 - \left(\frac{RT}{MU^2} \right) \left[\sqrt{1 + \frac{MU^2}{3RT}} - 1 \right] \right\}$$
 (5)

Solvation number: $S_n = \frac{M_2}{M_1} \left[1 - \kappa_s / \kappa_{s1} \right] \left[\frac{100-X}{X} \right]$ (6)

Apparent molar compressibility: $\phi_k = 1000/m\rho_o (\rho_o \kappa_s - \rho \kappa_o) + (\kappa_o m / \rho_o)$ (7)

where κ_s , ρ and κ_o , ρ_o are represents the adiabatic compressibility and density of solution and solvent respectively, m is the molar concentration of solute.

Apparent molar volume: $\phi_v = (M/\rho) - [1000(\rho - \rho_o)/m\rho\rho_o]$ (8)

Some of these thermodynamic parameters are given in Table 4.

Table 4. Some acoustical parameters in DMF for pyrazolo quinazoline derivatives at different temperatures.

<i>Conc.</i> (<i>M</i>)	$b \times 10^5$ ($m^3 \cdot mol^{-1}$)	$L_f \times 10^{11}$ <i>m</i>	$Z \times 10^6$ $Kg \cdot s^{-1} \cdot m^{-2}$	$b \times 10^5$ ($m^3 \cdot mol^{-1}$)	$L_f \times 10^{11}$ <i>m</i>	$Z \times 10^6$ $kg \cdot s^{-1} \cdot m^{-2}$
298.15 K						
<i>K-1</i>				<i>K-2</i>		
0.00	7.3019	4.5925	1.3760	7.3019	4.5925	1.3760
0.01	7.4280	4.5748	1.3825	7.4381	4.5734	1.3826
0.02	7.5544	4.5668	1.3859	7.5622	4.5612	1.3881
0.04	7.8065	4.5532	1.3918	7.8351	4.5474	1.3936
0.06	8.0594	4.5436	1.3963	8.1012	4.5338	1.3994
0.08	8.3154	4.5357	1.3999	8.3750	4.5220	1.4040
0.10	8.5746	4.5276	1.4033	8.6565	4.5095	1.4081
<i>K-3</i>				<i>K-4</i>		
0.00	7.3019	4.5925	1.3760	7.3019	4.5925	1.3760
0.01	7.4208	4.5709	1.3846	7.4623	4.5699	1.3848
0.02	7.5535	4.5616	1.3882	7.6285	4.5543	1.3909
0.04	7.8254	4.5507	1.3923	7.9542	4.5339	1.4000
0.06	8.0949	4.5392	1.3968	8.2770	4.5178	1.4077
0.08	8.3541	4.5313	1.4007	8.5988	4.5027	1.4148
0.10	8.6299	4.5221	1.4038	8.9480	4.4886	1.4196
<i>K-5</i>						
0.00	7.3019	4.5925	1.3760			
0.01	7.4179	4.5751	1.3825			
0.02	7.5371	4.5663	1.3861			
0.04	7.7769	4.5530	1.3916			
0.06	8.0297	4.5426	1.3951			
0.08	8.2699	4.5316	1.3997			
0.10	8.5186	4.5204	1.4037			
308.15 K						
<i>K-1</i>				<i>K-2</i>		
0.00	7.3626	4.7426	1.3257	7.3626	4.7426	1.3257
0.01	7.4873	4.7181	1.3340	7.4956	4.7199	1.3334
0.02	7.6166	4.7112	1.3369	7.6356	4.7077	1.3375
0.04	7.8731	4.6983	1.3423	7.9080	4.6925	1.3435
0.06	8.1303	4.6896	1.3463	8.1706	4.6771	1.3502
0.08	8.3870	4.6797	1.3506	8.4461	4.6645	1.3549
0.10	8.6506	4.6708	1.3540	8.7137	4.6511	1.3603
<i>K-3</i>				<i>K-4</i>		
0.00	7.3626	4.7426	1.3257	7.3626	4.7426	1.3257

0.01	7.4944	4.7207	1.3330	7.5261	4.7168	1.3349
0.02	7.6296	4.7094	1.3370	7.6956	4.6987	1.3413
0.04	7.8996	4.6965	1.3420	8.0274	4.6779	1.3501
0.06	8.1656	4.6829	1.3475	8.3566	4.6575	1.3586
0.08	8.4273	4.6738	1.3517	8.6853	4.6415	1.3656
0.10	8.6936	4.6645	1.3556	9.0415	4.6271	1.3701

K-5

0.00	7.3626	4.7426	1.3257			
0.01	7.4884	4.7228	1.3319			
0.02	7.6097	4.7132	1.3355			
0.04	7.8506	4.6982	1.3415			
0.06	8.1011	4.6867	1.3456			
0.08	8.3450	4.6738	1.3506			
0.10	8.5930	4.6627	1.3546			

318.15 K

K-1				K-2		
0.00	7.4247	4.9006	1.2763	7.4247	4.9006	1.2763
0.01	7.5553	4.8729	1.2847	7.5634	4.8753	1.2840
0.02	7.6873	4.8646	1.2878	7.6996	4.8604	1.2891
0.04	7.9488	4.8511	1.2931	7.9781	4.8426	1.2954
0.06	8.2113	4.8400	1.2976	8.2576	4.8269	1.3010
0.08	8.4773	4.8301	1.3013	8.5331	4.8111	1.3067
0.10	8.7408	4.8199	1.3052	8.8013	4.7958	1.3126

K-3

K-3				K-4		
0.00	7.4247	4.9006	1.2763	7.4247	4.9006	1.2763
0.01	7.5452	4.8705	1.2866	7.5917	4.8692	1.2865
0.02	7.6856	4.8628	1.2891	7.7646	4.8485	1.2932
0.04	7.9680	4.8478	1.2938	8.1028	4.8256	1.3021
0.06	8.2491	4.8351	1.2979	8.4340	4.8062	1.3101
0.08	8.5182	4.8253	1.3021	8.7687	4.7878	1.3174
0.10	8.7920	4.8139	1.3062	9.1227	4.7752	1.3217

K-5

0.00	7.4247	4.9006	1.2763			
0.01	7.5490	4.8761	1.2837			
0.02	7.6758	4.8675	1.2866			
0.04	7.9273	4.8509	1.2922			
0.06	8.1834	4.8383	1.2964			
0.08	8.4330	4.8242	1.3013			
0.10	8.6896	4.8130	1.3049			

It is clear from the Figure 4 that ultrasonic velocity increases with concentration for all the compounds at all the studied temperatures. For all the compounds, the ultrasonic velocity is found to increase with concentration and decrease with temperature. The velocity is related

to intermolecular free path length. Table 4 shows that as concentration increases, intermolecular free length (L_f) decreases. Thus, ultrasonic velocity is reverse of intermolecular free length (L_f). The decrease of intermolecular free length (L_f) with increase of concentration suggests the decrease of distance between solute and solvent molecules due to solute-solvent interactions which causes velocity to increase. Further, as temperature increases, ultrasonic velocity (U) decreases whereas intermolecular free length (L_f) increases as shown in Tables 3 and 4 respectively. Thus, temperature plays an important role in molecular interactions in solutions.

The existence of solute-solvent interactions in studied solutions is further confirmed by decrease of adiabatic compressibility with increase in concentration, shown in Figure 5. The compressibility of the solution is mainly due to free solvent molecules around solute molecules. So, when there is strong interaction between solvent and compound molecules, compressibility decreases which is the case in present study. By increase in concentration of solute (compound), molecular associations are enhanced and newly formed aggregates cause adiabatic compressibility to decrease. Furthermore, κ_s also increases with increase in temperature.

The solute-solvent interactions in studied solutions are further confirmed by acoustical impedance (Z) which are found to increase with increase in concentration (Tables 4). Similar behavior was also observed by Aswale et al. This acoustical parameter also decreases with temperature due to decrease in solute-solvent interactions. It is observed from the Table 4 that the values of vander Waals constant (b) is found to be vary linearly with concentration. The linear variation suggests the absence of complex structure in the solution.

Figure 6 show values of internal pressure in different solutions. It is observed that as concentration of solute and temperature increases, internal pressure (π) decreases for all the compounds. The internal pressure is a measure of cohesive energy and decrease of this cohesive energy suggests the presence of solute-solute interactions also in the system. However, solute-solvent interactions dominate as suggested by other acoustical properties.

The type of interactions between solute and solvent molecules can also be confirmed by solvation number (S_n). which gives the information about structure forming tendency or structure breaking tendency of a compound in solutions. Figure 7 shows the variation of solvation number with concentration for all the compounds at different temperatures in DMF. It is observed that for all the compounds, the solvation numbers are positive indicating thereby appreciable solvation of compounds. This suggests structure forming tendency of compounds in DMF solutions which again confirms existence of solute-solvent interactions. As solute i.e., compound concentration increases, solute-solvent interactions also increases due to increase in aggregation of molecules i.e., structure forming tendency of solute. So, there is increment in solvation number with concentration [27].

The structure forming or structure breaking tendency of a compound in a solution depends on the nature of compound. In the studied compounds, central moiety is same for all but substitutions are different. Thus, nature of different substituent groups plays an important role. The electronegativity, polarity, positive resonating effect (+R), positive hyper conjugation effect (+H), negative inductive effect (-I) of different groups affect the interactions in solutions.

With increase in temperature, interactions are disturbed due to increase in molecular movements resulting in weak interactions between compound and solvent molecules. This causes decrease in solvation number (S_n) with increase in temperature.

Thus, all acoustical parameters suggest that as solute i.e., compound concentration increases, solute-solvent interactions increases which causes increase in aggregation of molecules i.e., structure forming tendency of compound in solutions of studied solvents. The interactions in solutions are affected by temperature, concentration, structure of compounds and solvent. Further, it is observed from Figures 4 that ultrasonic velocity is maximum for K-4 and minimum for K-1, indicating thereby maximum molecular interactions for K-4 and minimum for K-1. The type and magnitude of interaction depends upon structure of compound as well as solvent. In the present study, solvent is same for all the compounds so different structure is responsible for magnitude of molecular interactions. For all the compounds, central moiety is same but side chains are different. Table 1 shows that compound containing 3-bromo group (K-4) exhibited maximum molecular interaction in DMF whereas minimum molecular interaction is observed for K-1 containing 4-cyano group. This suggests that electro negativity of groups play an important role in DMF solution of studied compounds. Lower the electro negativity, maximum is the molecular interaction which reflects in all the acoustical parameters. The reverse nature is observed for adiabatic compressibility as shown in Figure 5.

The type and magnitude of interactions can also be confirmed by apparent molar properties. The apparent molar compressibility (ϕ_k) and apparent molar volume (ϕ_v) of solutions are fitted to Gucker's (equation 9) and Masson relations (equation 10) respectively.

$$\phi_k = \phi_k^{\circ} + S_k m^{1/2} \quad \dots (9)$$

and

$$\phi_v = \phi_v^{\circ} + S_v m^{1/2} \quad \dots (10)$$

where ϕ_k° and ϕ_v° are the limiting apparent molar compressibility limiting apparent molar volume at infinite dilutions. S_k and S_v are interaction parameters. S_k is measure of solute-solute interactions whereas S_v is measure of solute-solvent interaction [28, 29].

The values of ϕ_k° and S_k (of equation 9) and of ϕ_v° and S_v (of equation 10) are calculated by the least square method and are reported in Table 5.

The interactions in solutions can also be suggested by Bachem's relation [30], which is:

$$\kappa_s = \kappa_s^0 + AC + BC^{3/2} \quad \dots (11)$$

where A and B are constants, C is molar concentration of solutions, and κ_s and κ_s^0 are adiabatic compressibilities of the solution and solvent respectively. The constants A and B have been determined from the intercept and slope of the plots $(\kappa_s - \kappa_s^0)/C$ verses $C^{1/2}$ and are given in Table 5.

As shown in Table 5, values of A, ϕ_k° and ϕ_v° values are negative whereas B, S_k and S_v values are positive for all the synthesized compounds at different temperatures.

There are two factors that contribute to ϕ_k° : large organic compound can have some solvent intrinsic compressibility (positive effect) due to the intermolecular free space. This causes solution to be more compressible [31] and (ii) penetration or negative effect of the solvent molecules into the intra-compound free space due to the interaction of compounds with the neighboring solvent molecules. Thus, the intrinsic effect of solute i.e., compound is essentially an electrostriction effect causing constriction of solution volume resulting in a less compressible medium.

The negative limiting apparent molar isentropic compressibility for the solutions can be attributed to the predominance of a penetration effect of solvent molecules into the intra molecular free space of compound [32]. Thus, the solvent surrounding the compound causes greater resistance to compression than the bulk solvent resulting in negative limiting apparent molar isentropic compressibility and positive S_k . As temperature increases, resistance decreases which causes ϕ_k^0 values to be more negative with increasing temperature.

The electrostriction effect in studied solutions i.e., the decrease in compressibility is further reflected by negative ϕ_v^0 values. S_v is a coefficient which provides information regarding solute-solute interactions [33]. The sign of S_v can be used to interpret the nature of interaction occurring in solutions. Table 5 shows the positive values of S_v for all the compounds which suggest interaction of compound molecules in solutions [34]. The values of S_v increases with temperature which confirms that due to thermal agitation solute-solvent interactions are decreased.

Thus, negative ϕ_k^0 , ϕ_v^0 and positive S_k , S_v values indicate the structure forming tendency of compounds in DMF solutions. This is again supported by Bechem's constants A and B (Table 5). The negative A and positive B for all the compounds confirms solute-solvent interactions in all the solutions of compounds [35].

Table 5. Coefficients of equations (9), (10) and (11) for pyrazolo quinazoline derivatives at different temperatures.

<i>Coefficient</i>	<i>K-1</i>	<i>K-2</i>	<i>K-3</i>	<i>K-4</i>	<i>K-5</i>
298.15 K					
<i>A</i>	-3.75	-3.1	-3.2	-4.4	-2.55
<i>B</i>	6.64	4.57	5.71	6.42	3.57
$\phi_k^0 \times 10^{-2} N^{-1} mol^{-1}$	-4.45	-4.7	-4.15	-6.2	-5.75
$S_k \times 10^{-13} m^3 . mol^{-1}$	8.18	7.90	7.14	11.0	13.5
$\phi_v^0 N^{-1} m^3 mol^{-1}$	-3.15	-139.0	-200.0	-266.0	-138.0
$S_v \times 10^8 N^{-1} m^{-1} . mol^{-3/2}$	6.92	138.14	374.54	267.25	188.85
308.15 K					
<i>A</i>	-4.1	-3.7	-3.75	-5.4	-2.9
<i>B</i>	7.81	5.71	6.85	8.42	4.28
$\phi_k^0 \times 10^{-2} N^{-1} mol^{-1}$	-5.4	-5.4	-4.85	-7.2	-5.90
$S_k \times 10^{-13} m^3 . mol^{-1}$	10.5	8.75	8.25	12.14	12.5
$\phi_v^0 N^{-1} m^3 mol^{-1}$	-4.24	-172.0	-225.0	-275.0	-173.0
$S_v \times 10^8 N^{-1} m^{-1} . mol^{-3/2}$	8.05	176.16	511.0	291.05	267.45

318.15 K					
<i>A</i>	-4.65	-4.2	-4.3	-6.4	-3.75
<i>B</i>	9	6.25	7.43	10.57	5.42
$\phi_k^\circ \times 10^{-2} N^{-1} mol^{-1}$	-6.1	-6.05	-6.0	-8.65	-6.17
$S_k \times 10^{-13} m^3 \cdot mol^{-1}$	11.87	9.54	11.27	15.54	11.88
$\phi_v^\circ N^{-1} m^3 mol^{-1}$	-4.87	-187.0	-265.0	-285.0	-186.0
$S_v \times 10^8 N^{-1} m^{-1} \cdot mol^{-3/2}$	8.67	191.57	658.75	344.25	386.92

4. CONCLUSION

In the studied compounds, solute-solvent interactions increase with increase in concentration but decreases with temperature. The solute-solvent interactions are affected by electro negativity of different side chains present in the studied compounds. Out of all the studied compounds, the compound containing 4-CN group exhibited minimum solute-solvent interaction which is due to highly electro negative nature of cyano group.

Nomenclature:

<i>U</i>	Ultrasonic velocity
ρ	Density
η	Viscosity
κ_s	Adiabatic compressibility
<i>X</i>	Number of grams of solute in 100 gm of the solution
L_f	Intermolecular free length
ϕ_k	Apparent molar compressibility
ϕ_v	Apparent molar volume
ϕ_k°	Limiting apparent molar compressibility
ϕ_v°	Limiting apparent molar volume
S_k & S_v	Interaction parameters
S_n	Solvation number
<i>A</i> & <i>B</i>	Viscosity coefficients of Jones-Dole equation

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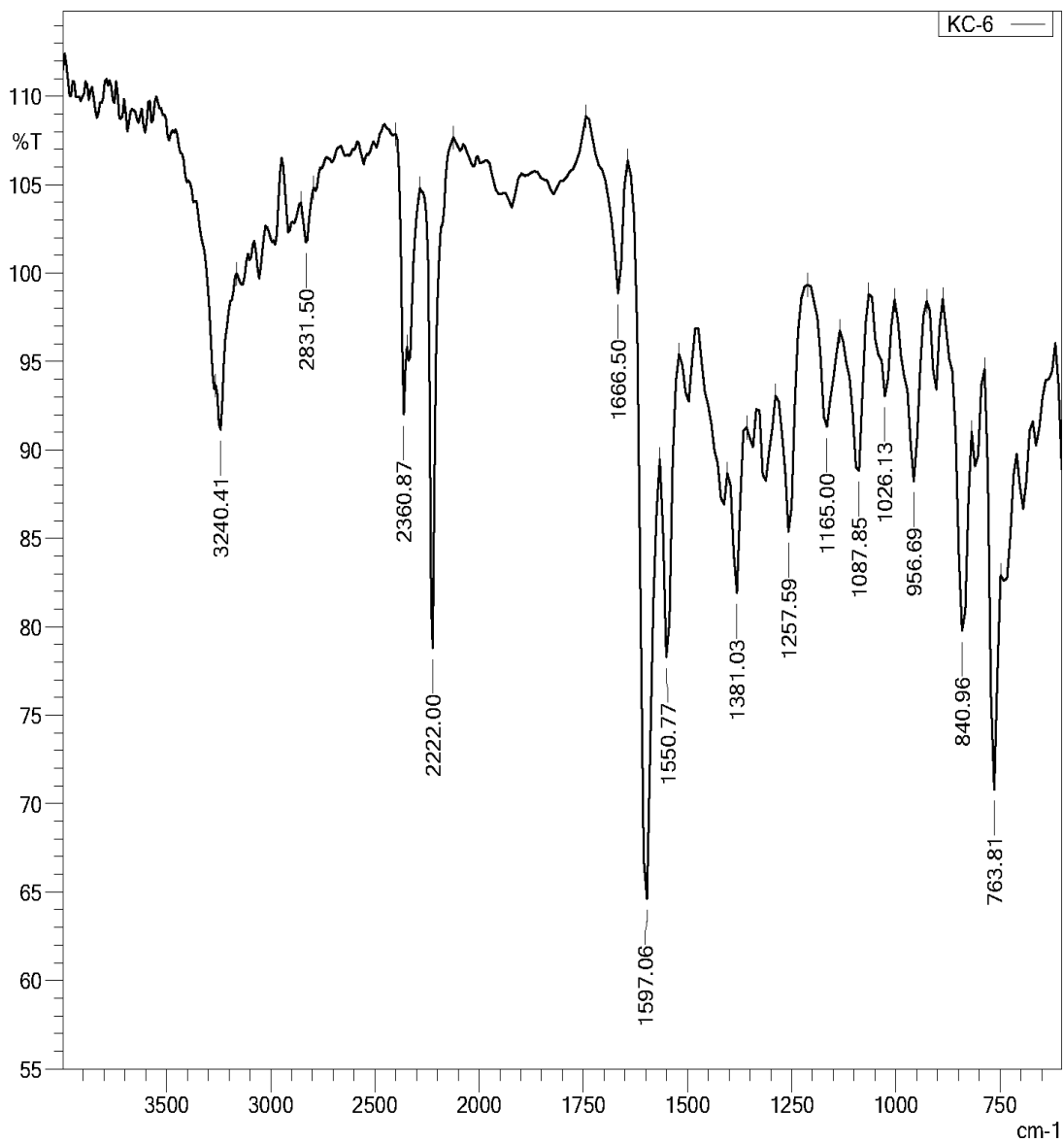


Figure 2. IR spectrum of compound K-1

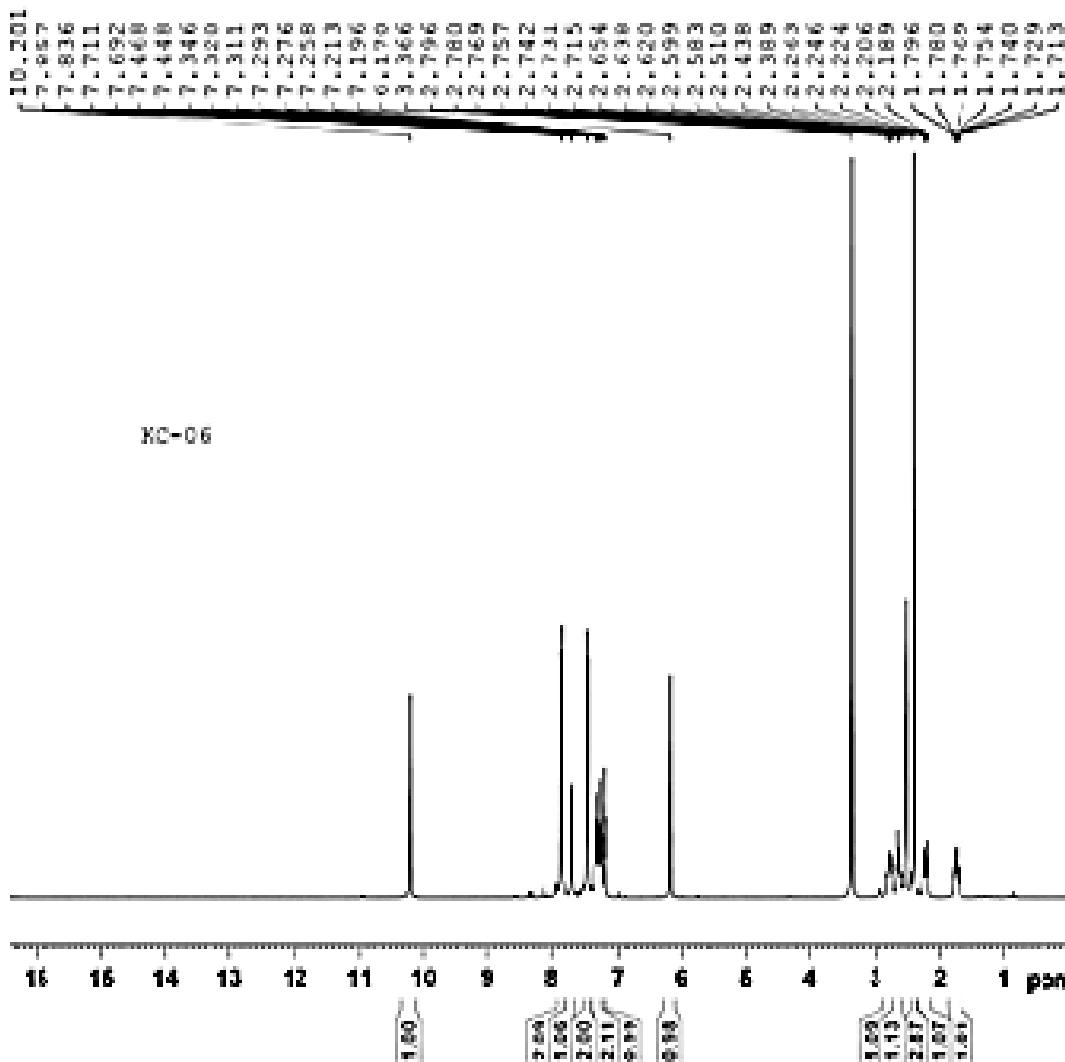


Figure 3. ¹H NMR spectrum of compound K-1

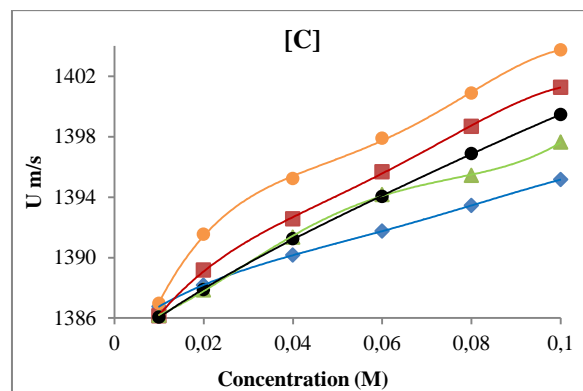
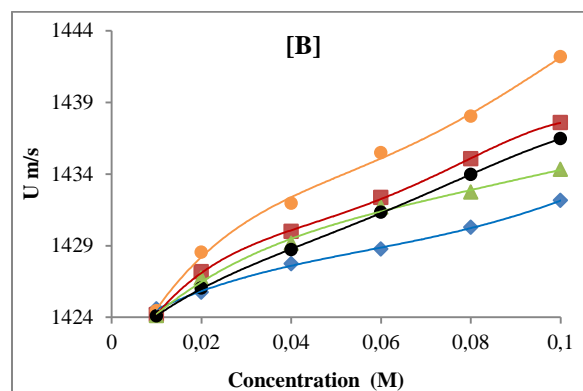
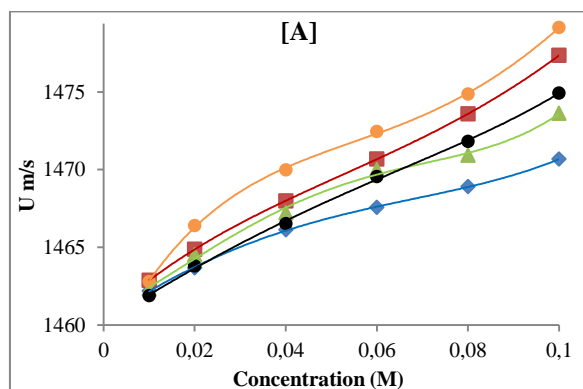


Figure 4. The variation of ultrasonic velocity with molar concentration of pyrazolo quinazoline derivatives in DMF at 298.15 K, 308.15 K and 318.15 K. K-1, ♦; K-2, ■; K-3, ▲; K-4, ●; K-5; ●

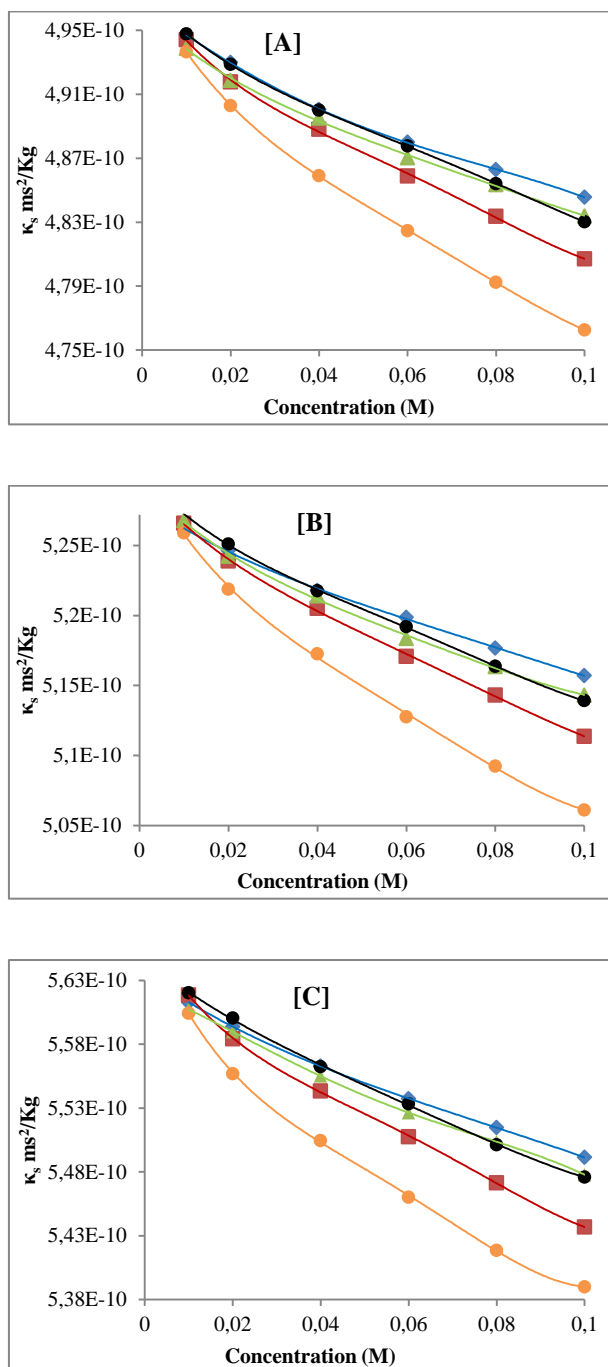


Figure 5. The variation of adiabatic compressibility (κ_s) with molar concentration of pyrazoloquinazoline derivatives in DMF at 298.15 K. K-1, \blacklozenge ; K-2, \blacksquare ; K-3, \blacktriangle ; K-4, \bullet ; K-5; \bullet

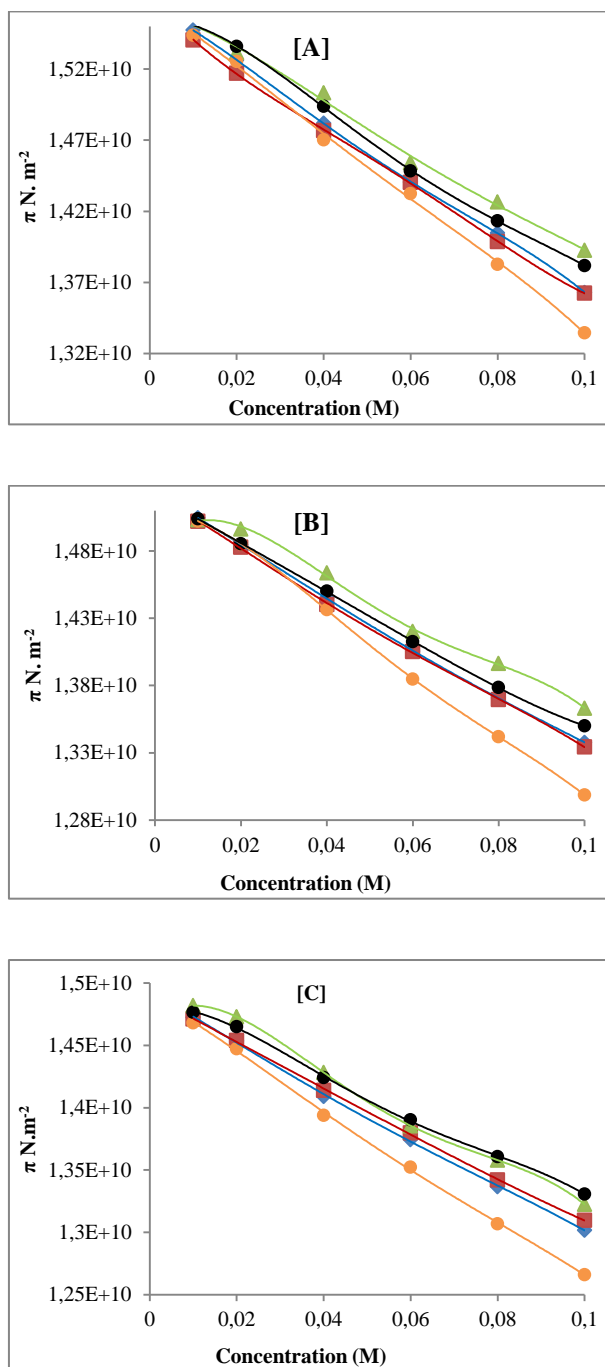


Figure 6. The variation of internal pressure (π) with molar concentration of pyrazolo quinazoline derivatives in DMF at 298.15 K, 308.15 K and 318.15 K. K-1, \diamond ; K-2, \blacksquare ; K-3, \blacktriangle ; K-4, \bullet ; K-5, \circ

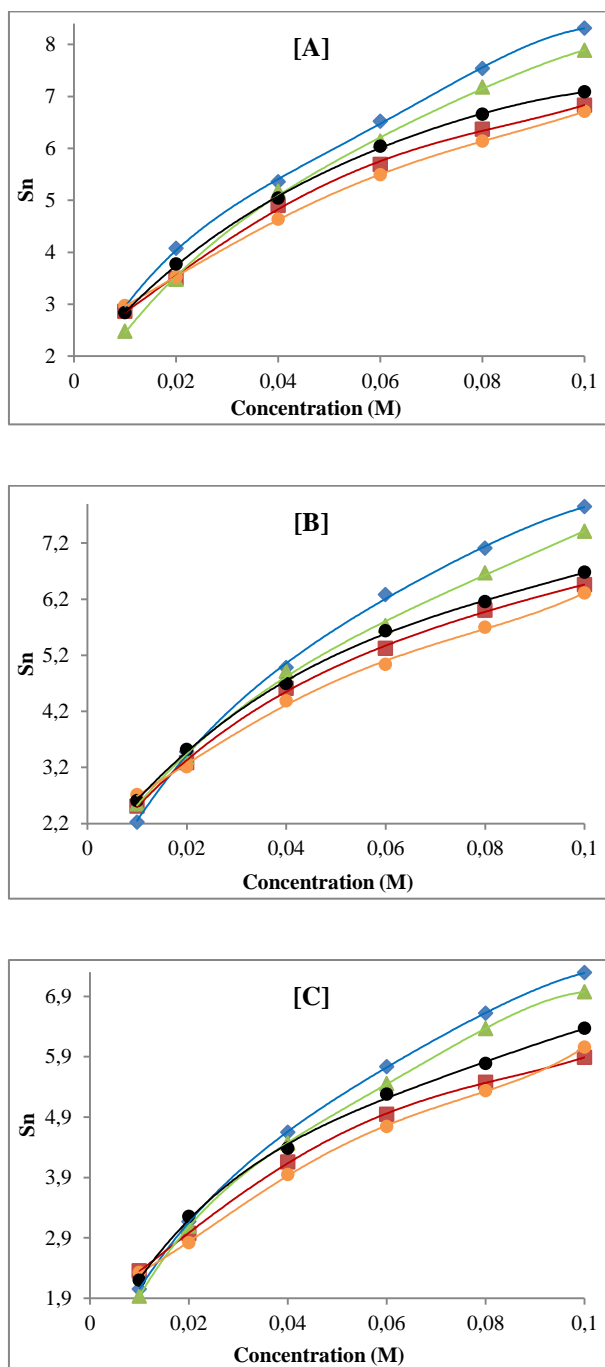


Figure 7. The variation of solvation number (S_n) with molar concentration pyrazoloquinazoline derivatives in DMF at 298.15 K. K-1, \blacklozenge ; K-2, \blacksquare ; K-3, \blacktriangle ; K-4, \bullet ; K-5; \bullet