

## Acoustical and Apparent Properties of Solutions of Some Cyanopyridine Derivatives

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### ABSTRACT

The acoustical parameters of some synthesized cyanopyridine derivatives have been studied from ultrasonic velocity and density measurements in solutions of different concentrations in dimethylsulphoxide and *N,N*-dimethylformamide at 298.15 K. From these experimental data, some acoustical and apparent properties were evaluated. The results provide useful information about compound-compound and compound-solvent interactions and are of significant help in understanding the behavior of synthesized compounds in solutions.

**Keywords:** Cyanopyridine derivatives, ultrasonic velocities, Dimethyl sulphoxide, *N, N*-dimethyl formamide etc.

### INTRODUCTION

Many naturally occurring and synthetic compounds bearing pyridine scaffold possess interesting biological properties [1]. In association with those, 2-amino-3-cyanopyridine derivatives possess biological activities such as antimicrobial [2], anticancer [3], anticonvulsant [4], antiviral [5], anti-HIV [6], antifungal [7], antimalarial [8] etc. Consequently, the synthesis of 2-amino-3-cyanopyridine derivatives keeps on attracting much interest in organic chemistry. Thus, for the present study, cyanopyridine derivatives are selected. The measurement of ultrasonic velocity has been successfully employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures [9-11]. The thermo acoustical parameters evaluated using ultrasonic velocity and density data for solutions are useful to understand physicochemical behavior of compounds and various types of molecular interactions [12-14]. In the present work, thermo acoustical parameters of solutions of some cyanopyridine derivatives have been reported in DMF and DMSO solutions at 298.15 K over a wide range of concentration.

### EXPERIMENTAL

#### Synthesis

#### *Synthesis of N-(naphthalene-1-yl)acetamide*

Equimolar mixture of 1-naphthyl amine and acetic anhydride in methanol was refluxed in

water bath for 2-3hrs using acetic acid as catalyst. The crude product was isolated and crystallized from absolute ethanol.

#### *Synthesis of 2-chloro benzo[h]quinoline-3-carbaldehyde*

*N*-(naphthalene-1-yl) acetamide was added in a mixture of vilsmeier-Haack reagent (prepared by drop wise addition of 6.5 ml POCl<sub>3</sub> in ice cooled 2ml DMF) and refluxed for 27 hrs. The reaction mixture was poured into ice and kept for overnight followed by neutralization using sodium bicarbonate. The crude product was isolated and crystallized from ethanol.

#### *Synthesis of 3-(2-chlorobenzo[h]quinolin-3-yl)-1-(4-methoxy-phenyl) prop-2-en-1-one*

To a well stirred solution of 2-chloro benzo[h]quinoline-3-carbaldehyde and *p*-methoxy-acetophenone in binary mixture of ethanol + DMF, 40% NaOH was added till the solution became basic. The reaction mixture was stirred for 48 hrs and the contents were poured into ice, acidified, filtered and crystallized from ethanol.

#### *Synthesis of 2-amino-4-(2-chlorobenzo[h]quinolin-3-yl)-6-(4-methoxy-phenyl) pyridine-3-carbonitrile (SC-1)*

A mixture of 3-(2-chlorobenzo[h]quinolin-3-yl)-1-(4-methoxy-phenyl) prop-2-en-1-one, malononitrile and ammonium acetate in ethanol was refluxed for 10-12 hrs. The content was

poured on crushed ice. The product obtained was filtered, washed with water and crystallized

from DMF. Similarly, other substituted cyano pyridines have been prepared. Figure 1 shows the reaction scheme.

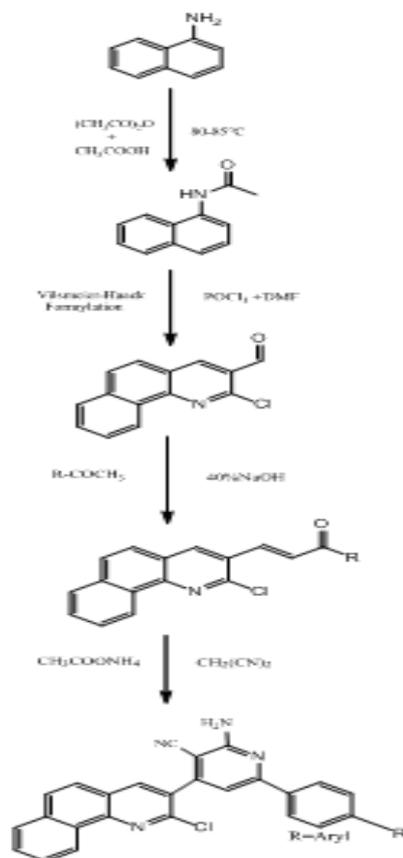


Fig1. Reaction Scheme

### SPECTROSCOPY STUDY

The characterization of all these compounds was done by IR, NMR and mass spectral data. The IR spectra were recorded by SHIMADZU-FTIR-8400 Spectrophotometer in the frequency range of 4000-400  $\text{cm}^{-1}$  by KBr powder method. The NMR spectra were recorded by BRUKER

Spectrometer (400 MHz) using internal reference TMS and solvent  $\text{CDCl}_3/\text{DMSO}$ . The Mass spectra were recorded by GCMS-SHIMADZU-QP2010. Table 1 shows the physical parameters of synthesized compounds.

Table1. Physical constants of synthesized compounds

No.	Code	Substitution R	Molecular Formula	Molecular Weight ( $\text{g.mol}^{-1}$ )	$R_f^*$ value	Melting point ( $^{\circ}\text{C}$ )	Yield (%)
1	SC-1	4- $\text{OCH}_3\text{-C}_6\text{H}_5\text{-}$	$\text{C}_{27}\text{H}_{17}\text{ClN}_4\text{O}$	436.08	0.59	221	70
2	SC-2	4- $\text{CH}_3\text{-C}_6\text{H}_5\text{-}$	$\text{C}_{26}\text{H}_{17}\text{ClN}_4$	420.8	0.56	180	68
3	SC-3	4- $\text{Br-C}_6\text{H}_5\text{-}$	$\text{C}_{25}\text{H}_{14}\text{BrClN}_4\text{O}$	485.7	0.63	214	71
4	SC-4	4- $\text{NH}_2\text{-C}_6\text{H}_5\text{-}$	$\text{C}_{25}\text{H}_{16}\text{ClN}_5$	421.8	0.69	208	65
5	SC-5	4- $\text{NO}_2\text{-C}_6\text{H}_5\text{-}$	$\text{C}_{25}\text{H}_{14}\text{ClN}_5\text{O}_2$	451.8	0.64	187	69

\*mobile phase for TLC, Ethyl acetate: Hexane: 3:7

### MEASUREMENTS OF DENSITY, VISCOSITY AND ULTRASOUND VELOCITY

The synthesized cyanopyridine derivatives were recrystallized before use. The selected solvents; *N,N*-dimethylformamide (DMF) and dimethylsulphoxide (DMSO) used for the

present study were of AR grade supplied by Spectrochem Pvt. Ltd. (Mumbai, India) and were purified according to the standard procedure [15]. The distilled DMF was stored over molecular sieves. The purity of both the solvents 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 $\mu$ m film) and was found to be more than 99.98%.

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

The densities and viscosities of pure solvents and solutions of cyanopyridine derivatives of different concentrations were measured at 298.15 K by using pycnometer, an Ubbelohde suspended level viscometer, with the uncertainties of  $\pm 0.0001$  g/cm<sup>3</sup> and 0.06 % respectively. The flow time of water and solutions were measured with a digital stop watch with an accuracy of  $\pm 0.01$  s (Model: RACER HS-10W). A single frequency (2 MHz) ultrasonic interferometer (Mittal Enterprises, Model F-81) with accuracy of  $\pm 0.03\%$  was used in the present work for measurement of ultrasonic velocities of pure solvents and solutions. A special thermostatic water bath arrangement was made for density, ultrasonic velocity and viscosity measurements, in which continuous stirring of water was carried out with the help of electric stirrer and temperature variation was maintained within  $\pm 0.01^\circ\text{C}$ .

## RESULTS AND DISCUSSION

Table 1 shows the physical constants of synthesized compounds with their side chain substitution.

### Spectral Data

**SC1: IR (KBr, cm<sup>-1</sup>):** N-H: 3314, C=C: 1514, C $\equiv$ N: 2195, C-Cl: 690. **<sup>1</sup>H NMR ( $\delta$  ppm):**- 3.83(s, 3H), 3.49 (s, 2H), 7.09-7.12(d, 2H), 7.5-7.54(t, 1H), 7.66-7.76(dd, 2H), 7.83-7.99(m, 2H), 8.07-8.10(m, 2H), 8.37(s, 1H), 8.51(d, 2H). **m/z:** 436.8, 422, 402, 385, 357, 338, 295, 247, 226, 218, 151, 108, 92, 78

**SC2: IR (KBr, cm<sup>-1</sup>):** N-H: 3348, C=C: 1518, C $\equiv$ N: 2201, C-Cl: 699. **<sup>1</sup>H NMR ( $\delta$  ppm):**- 2.75 (s, 3H), 3.55 (s, 2H), 7.08-7.16(d, 2H), 7.59-7.63(t, 1H), 7.81-7.85(dd, 2H), 8.04-8.08(m, 2H), 8.15-8.19(m, 2H), 8.34(s, 1H), 8.63(d, 2H). **m/z:** 420.8, 386, 369, 341, 295, 247, 218, 151, 108, 92, 78.

**SC3: IR (KBr, cm<sup>-1</sup>):**N-H: 3332, C=C : 1512, C $\equiv$ N: 2198, C-Cl: 709. **<sup>1</sup>H NMR ( $\delta$  ppm):**- 3.66 (s, 2H), 7.18-7.22(d, 2H), 7.51-7.67(t, 1H), 7.82-7.86(dd, 2H), 8.14-8.18(m, 2H), 8.38-8.44(m, 2H), 8.51(s, 1H), 8.63(d, 2H). **m/z:**

485.7 470, 451, 433, 406, 295, 218, 151, 108, 92, 78.

**SC4:IR (KBr, cm<sup>-1</sup>):** N-H: 3318, C=C : 1524, C $\equiv$ N: 2212, C-Cl: 718. **<sup>1</sup>H NMR ( $\delta$  ppm):**3.41 (s, 2H), 3.59(s, 2H), 7.01-7.06(d, 2H), 7.21-7.24(t, 1H), 7.61-7.64(dd, 2H), 7.83-7.94(m, 2H), 8.17-8.25(m, 2H), 8.31(s, 1H), 8.44(d, 2H). **m/z:** 421.8, 407, 387, 370, 323, 295, 247, 218, 151, 108, 92, 78.

**SC5:IR (KBr, cm<sup>-1</sup>):** N-H: 3321, C=C : 1504, C $\equiv$ N: 2208, C-Cl: 695. **<sup>1</sup>H NMR ( $\delta$  ppm):** 3.49 (s, 2H), 7.25-7.31(d, 2H), 7.59-7.61(t, 1H), 7.69-7.72(dd, 2H), 7.88-7.94(m, 2H), 8.17-8.23(m, 2H), 8.41(s, 1H), 8.56 (d, 2H). **m/z:** 451.8, 437, 435, 419, 417, 400, 353, 295, 247, 218, 151, 108, 92, 78.

The experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity ( $U$ ) of pure solvents and solutions of synthesized compounds are given in Table 2. To study molecular interactions of compounds in solutions, some acoustical and apparent parameters such as intermolecular free path length ( $L_f$ ), adiabatic compressibility ( $\kappa_s$ ), relaxation strength ( $r$ ), Rao's molar sound function ( $R_m$ ), Vander wall's constant ( $b$ ), molar compressibility ( $W$ ), solvation number ( $S_n$ ), apparent molar compressibility ( $\phi_k$ ) and apparent molar volume ( $\phi_v$ ) were evaluated using experimental data using following equations:

Intermolecular free path length:  $L_f = K_j \kappa_s^{1/2}$

where  $K_j$  is a temperature-dependent Jacobson's constant  $(93.875 + 0.375T) \times 10^{-8}$ .

Isentropic compressibility:  $\kappa_s = 1/U^2 \rho$

Relaxation Strength:  $r = 1 - (U/U_\infty)^2$  where  $U_\infty = 1.6 \times 10^5$  cm/s.

Rao's molar sound function:  $R_m = (M/\rho)U^{1/3}$  where  $M$  is the molecular weight of solution.

Vander wall's Constant:  $b = (M/\rho) (1-RT/MU^2 (\sqrt{(1+MU^2/3RT)}-1))$

Where  $R$  is gas constant and  $T$  is absolute temperature.

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

where  $X$  is the number of grams of solute in 100 gm of the solution.  $M_1$  and  $M_2$  are the molecular weights and  $\kappa_{s1}$  and  $\kappa_s$  are adiabatic

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compressibility of pure solvent and solute respectively.

Apparent molar compressibility:  $\phi_k = 1000/m\rho_0(\rho_0\kappa_s - \rho\kappa_0) + (\kappa_0 m/\rho_0)$

where  $\kappa_s$ ,  $\rho$  and  $\kappa_0$ ,  $\rho_0$  are represents the adiabatic compressibility and density of solution

and solvent respectively,  $m$  is the molar concentration of solute.

Apparent molar volume:  $\phi_v = (M/\rho) - [1000(\rho - \rho_0)/m\rho\rho_0]$

Some of these thermodynamic parameters are given in Table 3.

**Table 2.** The density ( $\rho$ ), ultrasonic velocity ( $U$ ) and viscosity ( $\eta$ ) of synthesized compounds in DMF and DMSO at 298.15 K

Conc. M	Density $\rho$ g.cm <sup>-3</sup>	Velocity $U$ . 10 <sup>-5</sup> cm.s <sup>-1</sup>	Viscosity $\eta$ .103 poise	Density $\rho$ g.cm-3	Velocity $U$ . 10 <sup>-5</sup> cm.s <sup>-1</sup>	Viscosity $\eta$ .10 <sup>3</sup> poise
<i>DMF</i>			<i>DMSO</i>			
<b>SC-1</b>						
<b>0.00</b>	0.9439	1.4616	7.7846	1.0959	1.4860	12.064
<b>0.01</b>	0.9447	1.4632	7.9614	1.0965	1.4868	12.3761
<b>0.02</b>	0.9455	1.4640	8.1278	1.0967	1.4880	12.5648
<b>0.04</b>	0.9463	1.4652	8.2713	1.0975	1.4900	12.9006
<b>0.06</b>	0.9474	1.4672	8.4643	1.0982	1.4924	13.2233
<b>0.08</b>	0.9529	1.4696	8.8012	1.1003	1.4948	13.5625
<b>0.10</b>	0.9587	1.4732	9.0865	1.1033	1.4980	14.0796
<b>SC-2</b>						
<b>0.01</b>	0.9455	1.4676	7.8486	1.0961	1.4880	12.6168
<b>0.02</b>	0.9467	1.4700	8.0185	1.0964	1.4904	12.9613
<b>0.04</b>	0.9483	1.4716	8.2941	1.0970	1.4928	13.2899
<b>0.06</b>	0.9507	1.4736	8.5820	1.0979	1.4964	13.9493
<b>0.08</b>	0.9549	1.4756	8.8945	1.0993	1.5056	15.1157
<b>0.10</b>	0.9598	1.4776	9.2214	1.1021	1.5192	17.0481
<b>SC-3</b>						
<b>0.01</b>	0.9488	1.4660	8.0118	1.0975	1.4876	12.3689
<b>0.02</b>	0.9528	1.4676	8.1842	1.0989	1.4896	12.7634
<b>0.04</b>	0.9593	1.4684	8.3849	1.1002	1.4928	13.2166
<b>0.06</b>	0.9615	1.4700	8.5547	1.1028	1.4972	13.9992
<b>0.08</b>	0.9629	1.4728	8.7309	1.1069	1.5048	14.9367
<b>0.10</b>	0.9691	1.4740	8.9509	1.1132	1.5164	16.3654
<b>SC-4</b>						
<b>0.01</b>	0.9471	1.4684	7.8619	1.0960	1.4904	12.8425
<b>0.02</b>	0.9482	1.4716	8.2253	1.0962	1.4928	13.3366
<b>0.04</b>	0.9497	1.4732	8.5783	1.0967	1.4964	14.1929
<b>0.06</b>	0.9513	1.4756	8.8343	1.0975	1.5016	14.9707
<b>0.08</b>	0.9532	1.4788	9.1655	1.0989	1.5116	16.3101
<b>0.10</b>	0.9551	1.4828	9.4017	1.1018	1.5268	18.3944
<b>SC-5</b>						
<b>0.01</b>	0.9445	1.4632	7.9840	1.0965	1.4884	13.2164
<b>0.02</b>	0.9454	1.4636	8.2825	1.0972	1.4904	13.6593
<b>0.04</b>	0.9467	1.4644	8.4813	1.0979	1.4936	14.6629
<b>0.06</b>	0.9480	1.4652	8.8811	1.0990	1.4984	15.8444
<b>0.08</b>	0.9542	1.4660	9.2296	1.1008	1.5044	17.0551
<b>0.10</b>	0.9609	1.4676	9.6921	1.1043	1.5120	19.5295

Figure 2 shows the variation of ultrasound velocity with concentration in DMF and DMSO.

It is observed that overall ultrasonic velocity increases with concentration for all the synthesized compounds in both the solvents.

Table 3 shows that intermolecular free length ( $L_f$ ) decreases with increase in concentration

although ultrasonic velocity increases with concentration.

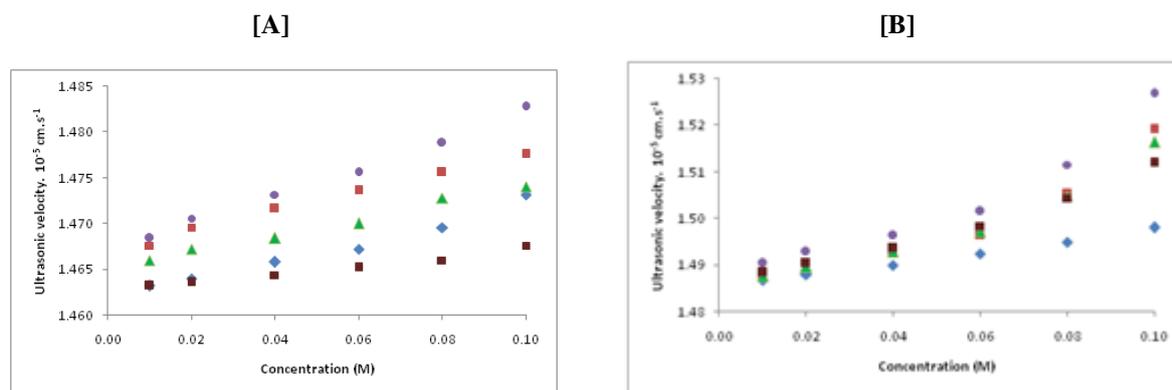
Thus, ultrasonic velocity is reverse of intermolecular free length. The decrease of intermolecular free length with increase of concentration suggests that the distance between solute and solvent molecules decrease due to

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increase in solute-solvent interactions, which causes velocity to increase.

**Fig2.** The variation of ultrasound velocity with concentration in [A] DMF and [B] DMSO.

◆: SC-1, ■: SC-2, ▲: SC-3, ●: SC-4, ■: SC-5.



**Table3.** Some acoustical parameters of synthesized compounds in DMF and DMSO.

Conc. (M)	$L_f A^0$	r	$R_m \cdot 10^{-3} \text{ cm}^{8/3} \cdot \text{s}^{-1/3}$	$b \text{ cm}^3 \cdot \text{mol}^{-1}$	$L_f A^0$	r	$R_m \cdot 10^{-3} \text{ cm}^{8/3} \cdot \text{s}^{-1/3}$	$b \text{ cm}^3 \cdot \text{mol}^{-1}$
<b>DMF</b>					<b>DMSO</b>			
<b>SC-1</b>								
0.00	1.4764	0.1655	4.0789	77.4323	1.3477	0.1374	3.7762	71.2914
0.01	1.4742	0.1637	4.1703	79.1396	1.3466	0.1365	3.8435	72.5502
0.02	1.4727	0.1628	4.2608	80.8411	1.3454	0.1351	3.9126	73.8340
0.04	1.4709	0.1614	4.4445	84.3037	1.3431	0.1328	4.0488	76.3690
0.06	1.4680	0.1591	4.6269	87.7233	1.3405	0.1300	4.1854	78.9045
0.08	1.4614	0.1564	4.7834	90.6414	1.3371	0.1272	4.3157	81.3167
0.10	1.4534	0.1522	4.9357	93.4522	1.3324	0.1234	4.4417	83.6313
<b>SC-2</b>								
0.01	1.4691	0.1587	4.1635	78.9311	1.3458	0.1351	3.8405	72.4735
0.02	1.4658	0.1559	4.2462	80.4546	1.3434	0.1323	3.9048	73.6478
0.04	1.4637	0.1541	4.4164	83.6489	1.3409	0.1295	4.0313	75.9925
0.06	1.4605	0.1518	4.5813	86.7332	1.3371	0.1253	4.1575	78.3087
0.08	1.4498	0.1490	4.6926	88.7919	1.3281	0.1145	4.2867	80.5762
0.10	1.4467	0.1471	4.8496	91.7304	1.3145	0.0984	4.4135	82.7117
<b>SC-3</b>								
0.01	1.4682	0.1605	4.1789	79.2515	1.3453	0.1356	3.8588	72.8258
0.02	1.4635	0.1587	4.2785	81.1101	1.3426	0.1332	3.9422	74.3650
0.04	1.4577	0.1577	4.4777	84.8726	1.3389	0.1295	4.1131	77.5337
0.06	1.4545	0.1559	4.6962	88.9805	1.3334	0.1244	4.2789	80.5807
0.08	1.4506	0.1527	4.9189	93.1416	1.3242	0.1155	4.4397	83.4674
0.10	1.4448	0.1513	5.1077	96.6905	1.3104	0.1018	4.5918	86.1073
<b>SC-4</b>								
0.01	1.4671	0.1577	4.1575	78.8035	1.3437	0.1323	3.8433	72.4866
0.02	1.4630	0.1541	4.2416	80.3393	1.3414	0.1295	3.9083	73.6744
0.04	1.4603	0.1522	4.4077	83.4552	1.3378	0.1253	4.0371	76.0400
0.06	1.4567	0.1495	4.5732	86.5409	1.3327	0.1192	4.1660	78.3779
0.08	1.4521	0.1458	4.7369	89.5731	1.3231	0.1074	4.2968	80.6595
0.10	1.4467	0.1411	4.9003	92.5806	1.3082	0.0894	4.4256	82.8003
<b>SC-5</b>								
0.01	1.4743	0.1637	4.1785	79.29365	1.3477	0.1346	3.8503	72.6511
0.02	1.4714	0.1623	4.4704	84.8099	1.3429	0.1286	4.0718	76.7420
0.04	1.4714	0.1623	4.4704	84.8099	1.3429	0.1286	4.0718	76.7420
0.06	1.4696	0.1614	4.6645	88.4761	1.3396	0.1230	4.2197	79.4442
0.08	1.4640	0.1605	4.8285	91.5716	1.3347	0.1159	4.3653	82.0762
0.10	1.4573	0.1587	4.9859	94.5212	1.3282	0.1070	4.5038	84.5389

**Fig3.** The variation of adiabatic compressibility with concentration in [A] DMF and [B] DMSO.

◆: SC-1, ■: SC-2, ▲: SC-3, ●: SC-4, ■: SC-5.

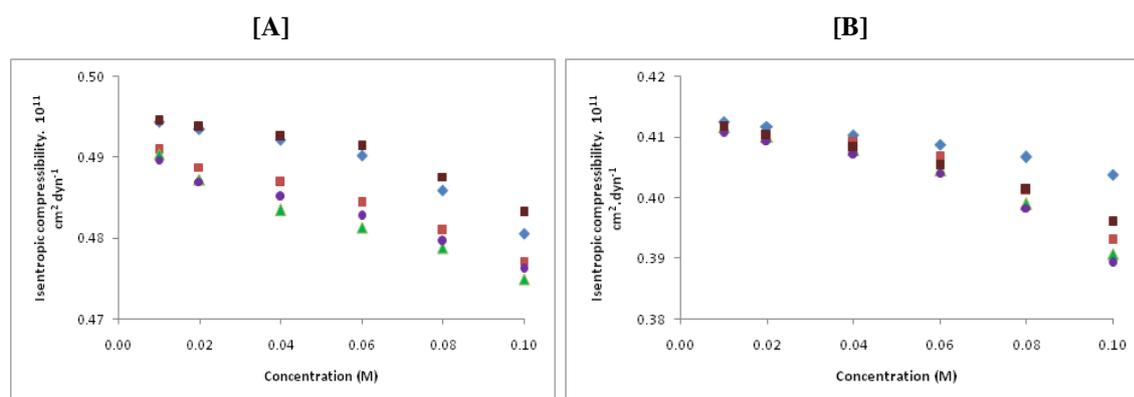


Figure 3 shows the variation of isentropic compressibility ( $\kappa_s$ ) with concentration for both the solvents. It is clear from Figure 3 that adiabatic compressibility decreases with increase in concentration. The decrease in isentropic compressibility is attributed to the fact that the cyano pyridine molecules in solutions are considerably ionized and these ions are surrounded by a layer of solvent molecules firmly bound and oriented toward the ions. The orientation of solvent molecules around the ions is attributed to the influence of the electrostatic field of the ions, which lowers the compressibility of the cyano pyridine solutions. The decrease in relaxation strength ( $r$ ) with concentration for all the compounds in Table 3 supports the existence of solute-solvent interactions in studied systems.

Table 3 shows the increase of molar sound function ( $R_m$ ) and Vander Waals constant ( $b$ ) with concentration for all the compounds. The correlation coefficients for these parameters are in the range of 0.9991- 0.9999. This linear

increase of these parameters suggests the absence of complex formation in these systems.

The type of interactions between solute and solvent molecules can also be suggested by a parameter solvation number ( $S_n$ ), which gives the information about structure forming tendency or structure breaking tendency of a compound in solutions. Figure 4 shows variation of solvation number of compounds with concentration in both the solvents. It is observed that for the studied compounds, the solvation numbers are positive, indicating thereby appreciable solvation of compounds. Thus, the studied compounds exhibited structure forming tendency due to solute-solvent interaction between solute and solvent molecules which causes an increase in solvation number. As solute concentration increases, solute-solvent interactions also increases which causes increase in aggregation of molecules i.e., structure forming tendency of solute. So, there is increment in solvation number with concentration.

**Table4.** Bachem's, Gucker's and Masson's constants of synthesized compounds in DMF and DMSO.

Compound	$A \times 10^{11} \text{ dyn}^{-1} \text{ cm}^{-3} \text{ mol}^{-1}$	$B \times 10^{11} \text{ dyn}^{-1} \text{ cm}^{-1/2} \text{ mol}^{-3/2}$	$\phi_K^0 \times 10^8 \text{ dyn}^{-1} \text{ mol}^{-1}$	$S_k \times 10^8 \text{ dyn}^{-1} \text{ cm}^{-3/2} \text{ mol}^{-3/2}$	$\phi_V^0 \times 10^8 \text{ cm}^3 \text{ mol}^{-1}$	$S_v \text{ cm}^3 \text{ mol}^{-1}$
<b>DMF</b>						
SC-1	-2.0689	5.7807	-0.0847	5.0287	-15.493	748.04
SC-2	-7.5476	27.399	-5.756	24.874	-91.203	1658.5
SC-3	-7.0976	18.52	-7.9125	25.837	-467.41	3988.2
SC-4	9.6435	35.182	-8.7746	35.161	-92.868	721.71
SC-5	1.7568	4.3109	-0.0078	6.3363	-4.916	365.07
<b>DMSO</b>						
SC-1	-0.6018	-0.6332	0.9600	0.6701	25.058	334.21
SC-2	-1.3757	1.2916	-0.4518	4.4506	55.352	-148.84
SC-3	-1.3526	-0.8861	-1.2129	6.4859	-93.938	1807.8
SC-4	-2.9966	6.6308	-1.7871	9.1544	65.591	-219.89
SC-5	-1.7205	1.8973	-0.4785	3.6792	50.06	370.9

Comparison of solvation number in the two solvents shows that in DMF, structure forming

tendency is much higher than that in DMSO. Further, in DMSO, for some compounds, there

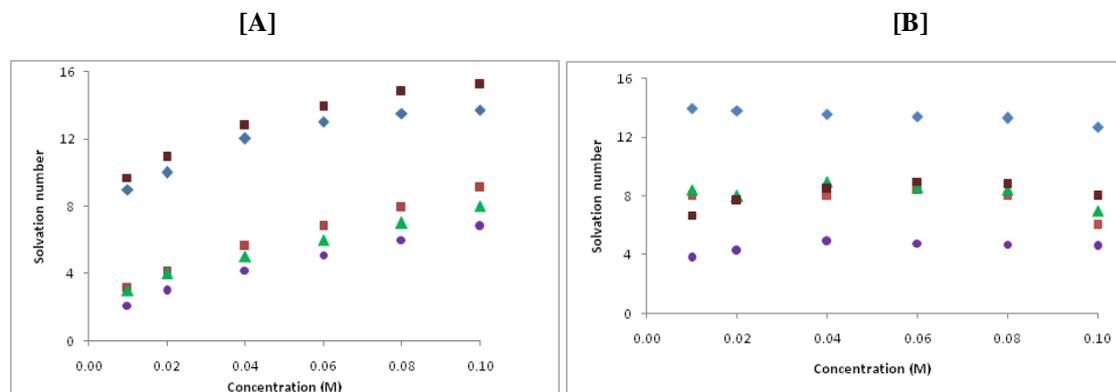
is decrease in solvation number with concentration although values are positive. This indicates that in DMSO, considerable amount of solute- solute interactions also exist.

The isentropic compressibility of all the solutions was also fitted to the following Bachem's relation [16]:

$$\kappa_s = \kappa_s^0 + AC + BC^{3/2}$$

**Fig4.** The variation of solvation number with concentration in [A] DMF and [B] DMSO.

◆: SC-1, ■: SC-2, ▲: SC-3, ●: SC-4, ■: SC-5.



Where A and B are constants, C is molar concentration of solutions, and  $\kappa_s$  and  $\kappa_s^0$  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  $(\kappa_s - \kappa_s^0)/C$  versus  $C^{1/2}$  and are given in Table 4.

The type and magnitude of interactions can also be confirmed by apparent molar properties. Apparent molar compressibility ( $\phi_k$ ) and apparent molar volume ( $\phi_v$ ) of solutions are fitted to Gucker's [17] and Masson [18] relations respectively.

$$\phi_k = \phi_k^0 + S_k m^{1/2}$$

and

$$\phi_v = \phi_v^0 + S_v m^{1/2}$$

where  $\phi_k^0$  and  $\phi_v^0$  are the limiting apparent molar compressibility limiting apparent molar volume at infinite dilutions.  $S_k$  and  $S_v$  are interaction parameters [19, 20].

The values of  $\phi_k^0$  and  $S_k$  and of  $\phi_v^0$  and  $S_v$  are calculated by the least square method and are reported in Table 4.

It is observed that for all the compounds in both the solvents, A values are negative whereas B values are mostly positive. The negative A and positive B again confirms the predominance of solute-solvent interactions in the system. In DMSO, for SC-1 and SC-3, negative B again confirms the existence of solute-solute interactions also in these systems. In a solution, when solute causes electrostriction in a solution, it causes decrease in compressibility which is

reflected by negative  $\phi_k^0$  values. For DMF, negative  $\phi_k^0$  and  $\phi_v^0$  values are due to solute-solvent interactions. However, in DMSO,  $\phi_k^0$  values are negative (except SC-1) whereas  $\phi_v^0$  values are mostly positive. This again confirms that in DMSO both solute-solute and solute-solvent interactions exist. This is further supported by  $S_k$  and  $S_v$  values. In DMF, both  $S_k$  and  $S_v$  values are positive and are higher than that in DMSO. For SC-2 and SC-4,  $S_v$  values are negative. The positive  $S_k$  and  $S_v$  values for all the compounds again indicate the structure forming tendency of compounds in solutions.

## CONCLUSION

Thus, it is concluded that although in both the solvents, solute-solvent interactions dominate, in DMSO solute-solute interactions also exist in considerable amount which is reflected in  $S_n$ ,  $S_k$  and  $S_v$  values. Thus, solute-solvent interactions are affected by electro negativity of the substitutions and type of solvent.

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