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Acoustical studies of some derivatives of 1,5-benzodiazepines at 298.15 K

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ABSTRACT

Some new derivatives of 1,5-Benzodiazepines have been synthesized and their structural characterizations are done by IR, NMR and Mass Spectral data. The ultrasonic velocity, density and viscosity of these synthesized compounds have been measured in dimethyl formamide and tetrahydrofuran at 298.15 K. From these experimental data, some acoustical parameters such as isentropic compressibility, intermolecular free path length, Rao's molar sound function, relaxation strength, solvation number etc., have been calculated which helps in understanding the molecular interactions occurring in these solutions.

Keywords: Benzodiazepine derivatives; ultrasonic Study; acoustical parameters; DMF; THF

1. INTRODUCTION

In recent years, much effort has been made to study ultrasonic properties of liquid mixtures[1-4]. However, scanty work has been done for solutions of organic compounds. Over the last few years, our research group is actively engaged in studying different types of organic compounds in various solvents[5-8]. In continuation of these investigations, the present paper reports acoustical properties of some Benzodiazepine derivatives in DMF and THF over entire concentration range at 298.15 K. The results are interpreted in terms of molecular interaction occurring in the solution.

2. EXPERIMENTAL

Five new Benzodiazepine derivatives have been synthesized. The reaction scheme is given in Figure 1. The compounds were recrystalized before use. The physical properties of synthesized compounds are given in Table 1 along with different substitutions. The DMF and THF used in the present work were of AR grade and were purified according to the standard procedure[9]. For all the compounds, solutions were prepared in DMF and THF over a wide range of concentrations and were stored in air tight bottles.

The computation of ultrasonic and thermodynamic properties requires the measurements of ultrasonic velocity viscosity and density. The densities (ρ) of pure solvents and their solutions were measured by using a single capillary pycnometer, made of borosil glass having a bulb capacity of 10 ml.

The ultrasonic velocity (U) of pure solvents and their solutions were measured by using single crystal variable path ultrasonic interferometer operating at 2 MHz. The accuracy of density and velocity are ±0.0001 g/cm^3 and ±0.1 % cm/sec respectively.

The viscosity (η) of pure solvents and solutions were measured by an Ubbelohde viscometer with an accuracy of 0.05 %. All the measurements were carried out at 298.15 K. The uncertainty of temperature is ±0.1 K and that of concentration is 0.0001 moles /dm^3.

3. RESULTS AND DISCUSSION

Table 2 shows the experimental data of density (ρ), viscosity (η) and ultrasonic velocity (U) of solutions of benzodiazepine derivatives at 298.15 K. The variation of ultrasound velocity (U) with concentration is shown in Figure 2. It is observed that in DMF and THF solutions, density, ultrasonic velocity and viscosity values increases with concentration for all the compounds.

From these experimental data of density, viscosity and ultrasound velocity of pure solvent and solutions, various acoustical parameters were calculated using the reported standard equations[8]. Figure 3 shows the variation of isentropic compressibility (κ_s) with concentration, which is reverse in nature than that of velocity (U). Further, Table 3 shows that intermolecular free length (L_f) and relaxation strength (r) also decreases with increase in concentration for all the compounds.

The increase of U and decrease of κ_s , L_f and r suggest aggregation of solvent molecules around solute molecules indicating thereby the presence of solute-solvent interactions.

Properties like molar sound function (R_m), molar compressibility (W) and Vander Waals constant (b) are observed to increase linearly with concentration for all the systems in both solvents. The linear variation of these acoustical properties indicates the absence of complex formation in these systems, as shown in Table 3 and Figure 4.

Figure 5 shows the variation of solvation number (S_n) with concentration. The solvation number (S_n) is a measure of structure forming or structure breaking tendency of a solute in solutions. In all the systems, S_n values are positive and increases with increase in concentration in both the solvents. The positive solvation number is due to structure forming tendency of these compounds in both the solvents.

Further, the apparent molar compressibilities (ϕ_k) of the solutions are fitted to Gucker's relation[10]

$$\phi_k = \phi^o_k + S_k \sqrt{C}$$

From the plot of ϕ_k verses $\sqrt{C}$, ϕ^o_k and S_k values are evaluated from the intercept and slope. The isentropic compressibility of all the solutions were also fitted to the following Bachem's relation[11]:

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

and values of A and B were evaluated from the intercept and slope respectively. All these values of intercept and slopes are given in Table 4.

It is evident from Table 4 that in both DMF and THF solutions, A and ϕ^o_k values are negative whereas B and S_k values are positive for all the compounds. The negative A and ϕ^o_k

and higher B values indicates solute-solvent interactions. The higher S_k values are also the indication of predominance of solute-solvent interactions.

Table 1. Physical constants of 1,5-benzodiazepines.

Sr. No.	Code	R	M.F.	M. Wt. (g/mol)	R_f Value	M.P. °C	Yield %
1	NKG-A	4-OH	$C_{24}H_{15}ClFN_3O$	415.8	0.74	248	61
2	NKG-B	4-CH_3	$C_{25}H_{17}ClFN_3$	413.9	0.82	186	55
3	NKG-C	4-Cl	$C_{24}H_{14}Cl_2FN_3$	434.4	0.59	232	52
4	NKG-D	2-OH	$C_{24}H_{15}ClFN_3O$	415.8	0.63	177	58
5	NKG-E	H	$C_{24}H_{15}ClFN_3$	399.8	0.70	182	62

Table 2. The density (ρ), ultrasonic velocity (U) and viscosity (η) of 1,5-benzodiazepine derivatives in DMF and THF at 298.15 K.

Conc. (M)	Density $g \cdot cm^{-3}$	Velocity x 10^{-5} $cm \cdot s^{-1}$	Viscosity x 10^3 poise	Density $g \cdot cm^{-3}$	Velocity x 10^{-5} $cm \cdot s^{-1}$	Viscosity x 10^3 poise
NKG-A	**DMF**			**THF**		
0.00	0.9449	1.4616	8.1418	0.8815	1.2780	4.6005
0.01	0.9472	1.4628	8.4259	0.8822	1.2796	4.7869
0.02	0.9503	1.4636	8.5980	0.8845	1.2804	4.9152
0.04	0.9546	1.4648	8.7095	0.8886	1.2812	5.1107
0.06	0.9559	1.4664	8.8547	0.8922	1.2820	5.2144
0.08	0.9576	1.4672	8.9514	0.8947	1.2828	5.3538
0.10	0.9587	1.4680	9.1318	0.8998	1.2844	5.4794
NKG-B						
0.01	0.9463	1.4640	8.3899	0.8828	1.2792	4.7752
0.02	0.9490	1.4648	8.5501	0.8845	1.2792	4.8816
0.04	0.9510	1.4664	8.6646	0.8863	1.2792	5.0001
0.06	0.9545	1.4668	8.7772	0.8884	1.2796	5.0983
0.08	0.9581	1.4676	8.8872	0.8915	1.2800	5.2442
0.10	0.9622	1.4700	9.0676	0.8957	1.2808	5.4317
NKG-C						
0.01	0.9508	1.4636	8.2449	0.8845	1.2796	4.7470
0.02	0.9520	1.4648	8.3881	0.8882	1.2804	4.8344
0.04	0.9551	1.4664	8.5244	0.8897	1.2828	4.9366
0.06	0.9575	1.4676	8.7484	0.8917	1.2844	5.0344
0.08	0.9604	1.4684	8.8680	0.8929	1.2860	5.1506
0.10	0.9660	1.4700	9.1156	0.8956	1.2888	5.2494

NKG-D						
0.01	0.9482	1.4632	8.2665	0.8837	1.2784	4.7502
0.02	0.9529	1.4648	8.4121	0.8864	1.2792	4.8996
0.04	0.9546	1.4664	8.5320	0.8892	1.2796	5.0353
0.06	0.9578	1.4676	8.7306	0.8930	1.2812	5.1285
0.08	0.9603	1.4696	8.8589	0.8946	1.2828	5.2095
0.10	0.9642	1.4712	9.0131	0.8973	1.2836	5.3314
NKG-E						
0.01	0.9464	1.4628	8.3267	0.8829	1.2780	4.6825
0.02	0.9489	1.4636	8.4690	0.8832	1.2792	4.7550
0.04	0.9523	1.4656	8.6362	0.8858	1.2800	4.8364
0.06	0.9563	1.4676	8.7614	0.8882	1.2816	4.9320
0.08	0.9591	1.4688	8.8478	0.8905	1.2836	5.0163
0.10	0.9612	1.4700	8.9972	0.8942	1.2852	5.1089

Table 3. Variation of some acoustical parameters with concentration of 1,5-benzodiazepine derivatives in DMF and THF at 298.15 K.

	DMF				**THF**			
Conc. (M)	**L_f (A^o)**	**R**	**$R_m.10^{-3}$ $cm^{-8/3}\cdot s^{-1/3}$**	**b $cm^3\cdot mol^{-1}$**	**L_f (A^o)**	**r**	**$R_m.10^{-3}$ $cm^{-8/3}\cdot s^{-1/3}$**	**b $cm^3\cdot mol^{-1}$**
NKG-A					**NKG-A**			
0.00	0.1476	0.1655	4.0746	77.3503	0.1747	0.3620	4.1205	81.8016
0.01	0.1473	0.1641	4.1496	78.7525	0.1754	0.3676	4.2097	83.6946
0.02	0.1469	0.1632	4.2198	80.0700	0.1762	0.3743	4.2943	85.5290
0.04	0.1465	0.1619	4.3662	82.8259	0.1759	0.3731	4.4853	89.3044
0.06	0.1462	0.1600	4.5260	85.8271	0.1742	0.3616	4.6896	93.0893
0.08	0.1460	0.1591	4.6820	88.7694	0.1733	0.3572	4.8771	96.7016
0.10	0.1459	0.1582	4.8405	91.7573	0.1723	0.3528	5.0482	99.9793
NKG-B					**NKG-B**			
0.01	0.1472	0.1628	4.1538	78.8120	0.1743	0.3600	4.2067	83.4684
0.02	0.1469	0.1619	4.2251	80.1504	0.1739	0.3588	4.2908	85.1117
0.04	0.1466	0.1600	4.3820	83.0963	0.1737	0.3576	4.4721	88.6803
0.06	0.1463	0.1596	4.5286	85.8671	0.1731	0.3556	4.6394	91.9492
0.08	0.1459	0.1587	4.6727	88.5846	0.1726	0.3540	4.7989	95.0724
0.10	0.1454	0.1559	4.8135	91.2038	0.1718	0.3508	4.9624	98.2285
NKG-C					**NKG-C**			
0.01	0.1469	0.1632	4.1424	78.6030	0.1746	0.3616	4.2448	84.2606
0.02	0.1467	0.1619	4.2293	80.2300	0.1744	0.3608	4.3672	86.6724
0.04	0.1463	0.1600	4.3977	83.3925	0.1742	0.3600	4.6120	91.5119
0.06	0.1460	0.1587	4.5672	86.5832	0.1737	0.3588	4.8420	96.0450
0.08	0.1457	0.1577	4.7317	89.6873	0.1734	0.3576	5.0860	100.8535
0.10	0.1451	0.1559	4.8791	92.4461	0.1727	0.3568	5.2882	104.8410

NKG-D					NKG-D			
0.01	0.1471	0.1637	4.1455	78.6677	0.1746	0.3616	4.2241	83.8492
0.02	0.1466	0.1619	4.2089	79.8429	0.1743	0.3604	4.3256	85.8374
0.04	0.1463	0.1600	4.3678	82.8260	0.1737	0.3580	4.5268	89.7749
0.06	0.1460	0.1587	4.5173	85.6383	0.1733	0.3568	4.7255	93.6850
0.08	0.1456	0.1564	4.6696	88.4849	0.1727	0.3556	4.9148	97.4074
0.10	0.1451	0.1545	4.8118	91.1459	0.1724	0.3544	5.1126	101.2966
NKG-E					**NKG-E**			
0.01	0.1473	0.1641	4.1461	78.6877	0.1745	0.3612	4.2235	83.8298
0.02	0.1471	0.1632	4.2123	79.9288	0.1743	0.3608	4.3231	85.7967
0.04	0.1470	0.1609	4.3507	82.5169	0.1739	0.3584	4.5359	89.9636
0.06	0.1461	0.1587	4.4840	85.0074	0.1733	0.3564	4.7320	93.8047
0.08	0.1458	0.1573	4.6209	87.5773	0.1728	0.3552	4.9250	97.5994
0.10	0.1455	0.1559	4.7601	90.1919	0.1723	0.3536	5.1136	101.2966

Table 4. Bachem's constants A, B, ϕ^{o}_{V}, S_v, ϕ^{o}_{k} and S_k of 1,5-benzodiazepine derivatives in DMF and THF at 298.15 K.

COMPOUNDS	$A \cdot 10^{11}$ $dyn^{-1}\cdot cm^{3}\cdot mol^{-1}$	$B \cdot 10^{11}$ $dyn^{-1}\cdot cm^{-1/2}\cdot mol^{-3/2}$	$\phi^{o}_{k} \cdot 10^{8}$ $dyn^{-1}\cdot mol^{-1}$	$S_k \cdot 10^{8}$ $dyn^{-1}cm^{-3/2}\cdot mol^{-3/2}$
DMF				
NKG-A	-2.82	5.33	-1.57	5.28
NKG-B	-2.90	5.36	-0.70	2.40
NKG-C	-4.20	12.05	-3.50	11.33
NKG-D	-2.33	2.00	-3.40	10.27
NKG-E	-1.97	1.85	-1.07	3.00
THF				
NKG-A	-2.79	2.30	-0.49	0.83
NKG-B	-3.16	5.46	-0.94	8.80
NKG-C	-2.83	1.97	-2.15	0.75
NKG-D	-0.72	3.33	-1.00	3.90
NKG-E	-2.91	3.50	-1.68	3.75

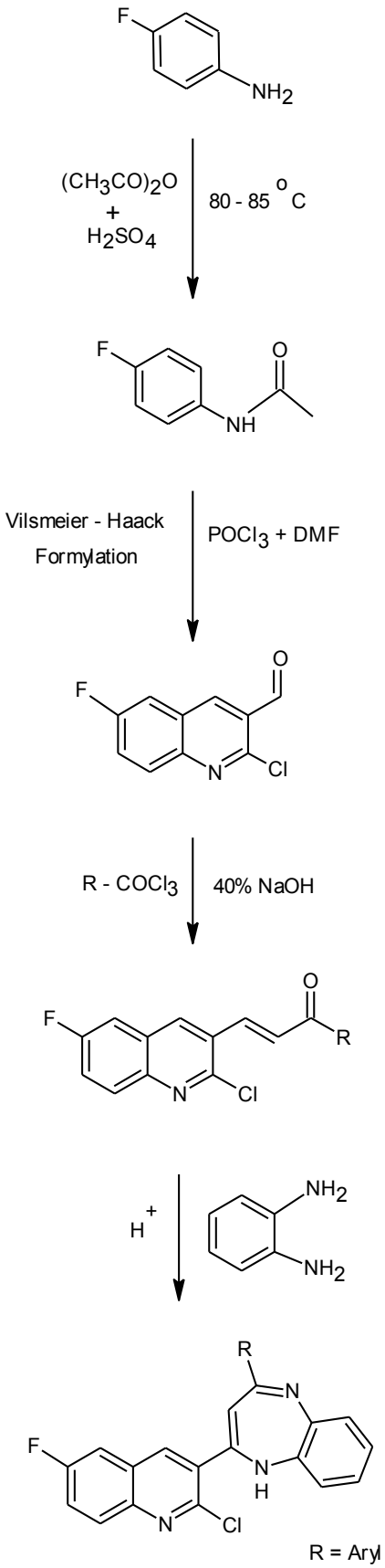


Figure 1. Reaction Scheme.

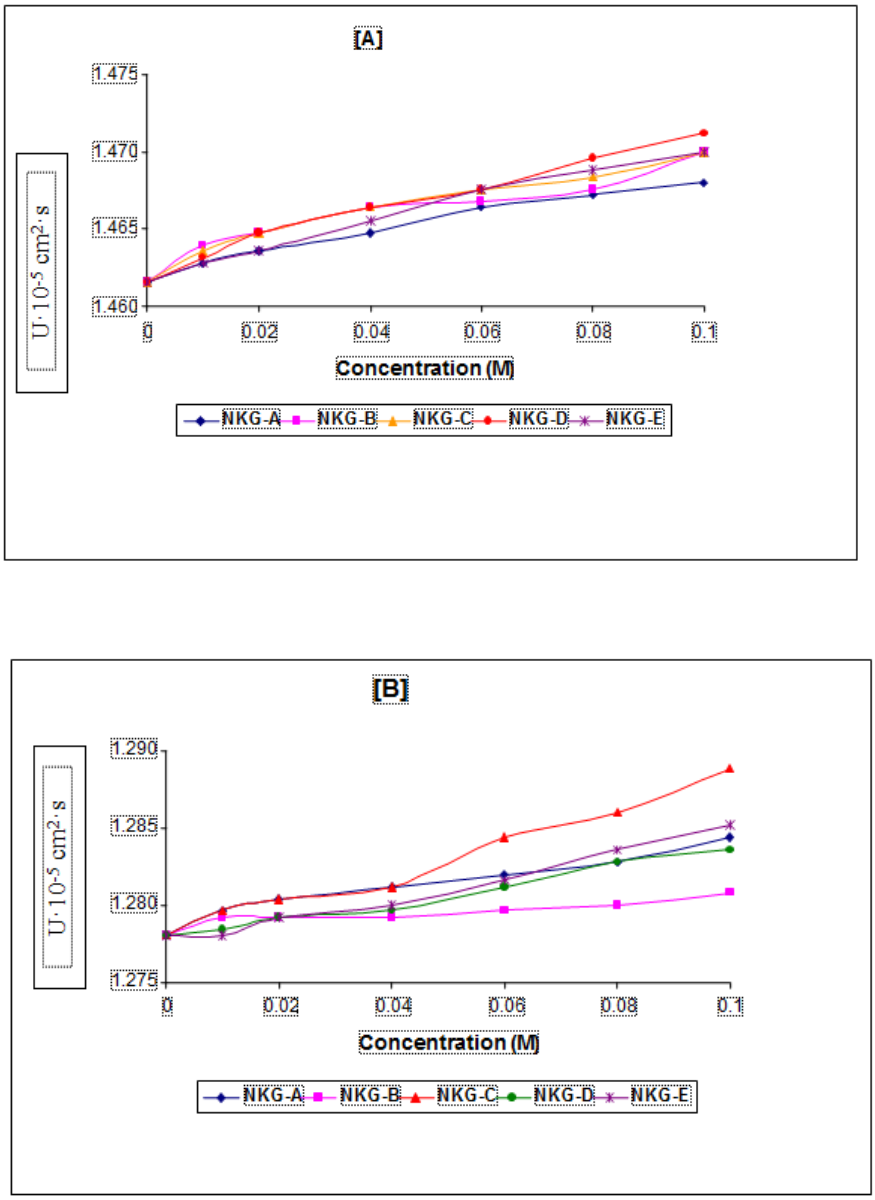


Figure 2. Variation of Ultrasonic velocity (U) with concentration of 1,5-benzodiazepine in (A) DMF and (B) THF at 298.15 K.

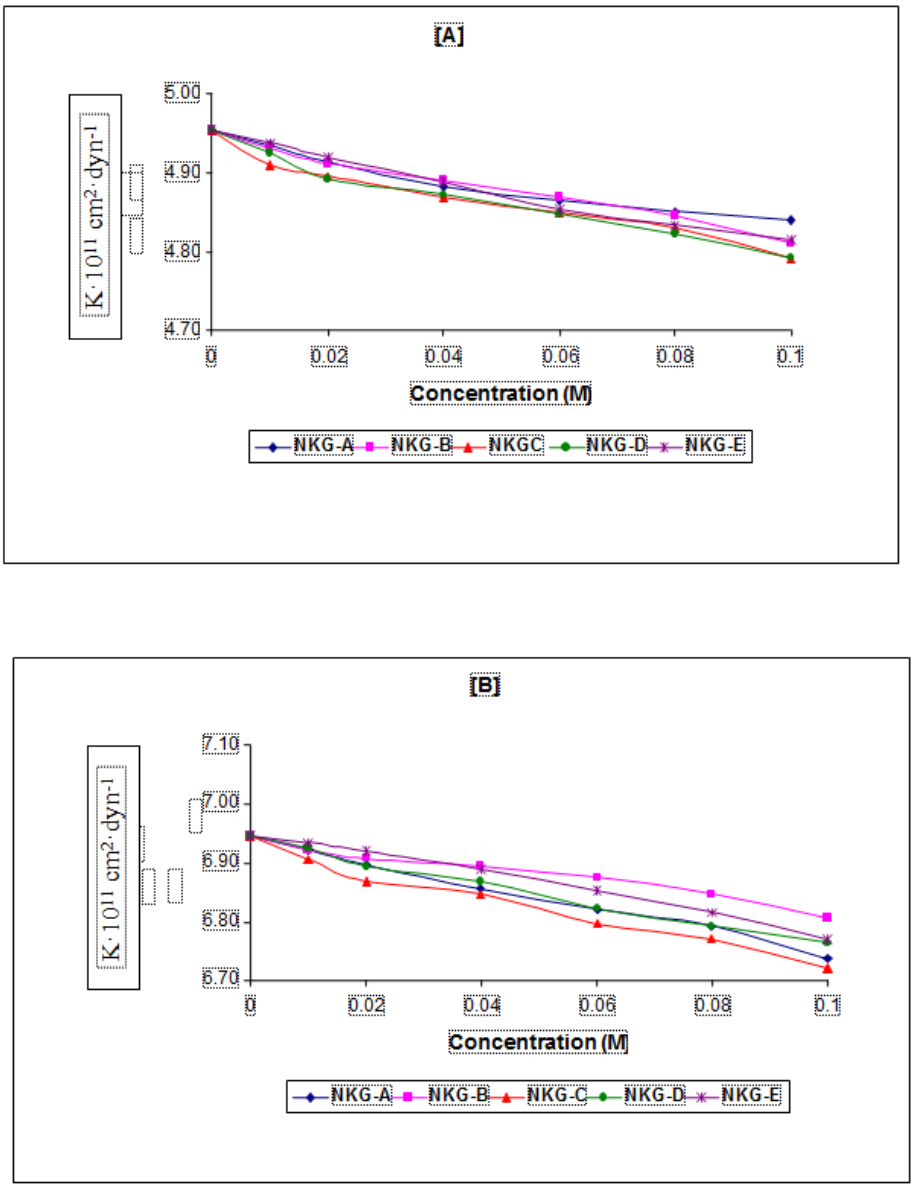


Figure 3. Variation of Isentropic compressibility (κ_s) with concentration of 1,5-benzodiazepine in (A) DMF and (B) THF at 298.15 K.

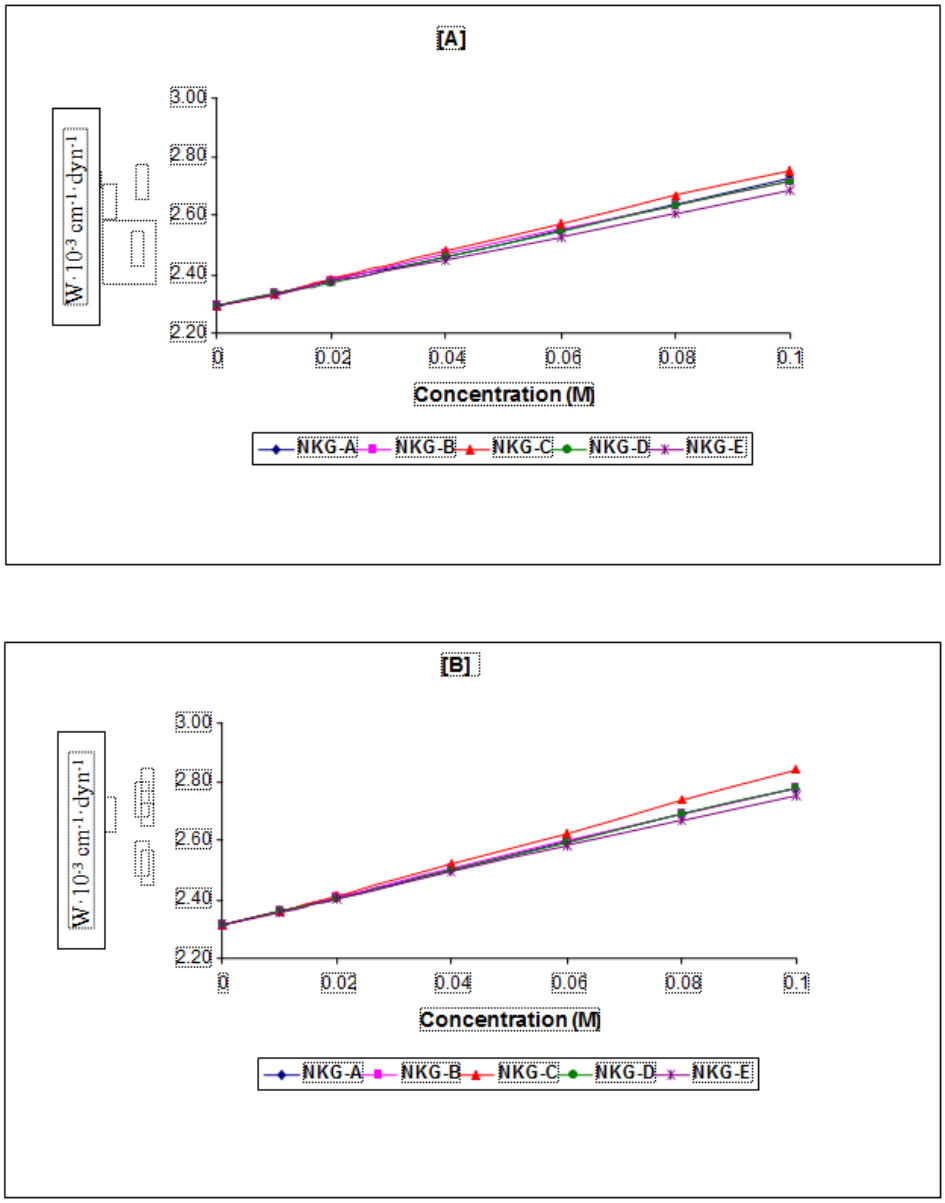
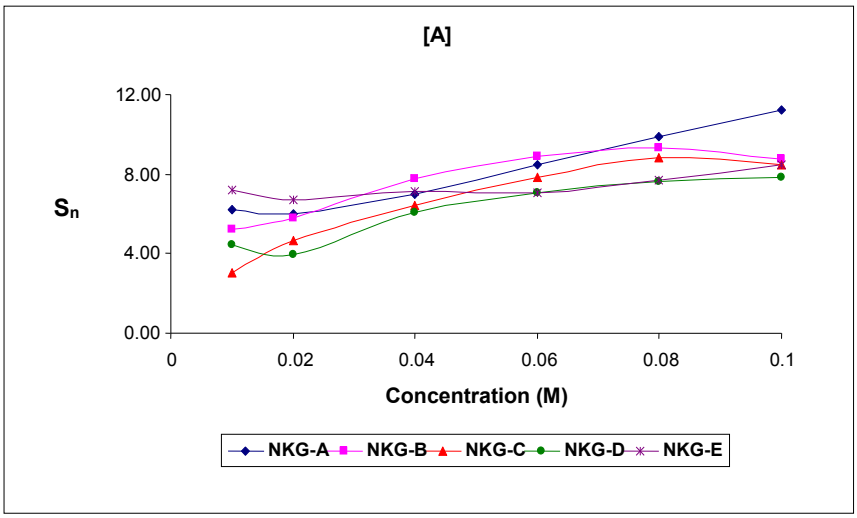


Figure 4. Variation of molar compressibility (W) with concentration of 1,5-benzodiazepine in (A) DMF and (B) THF at 298.15 K.



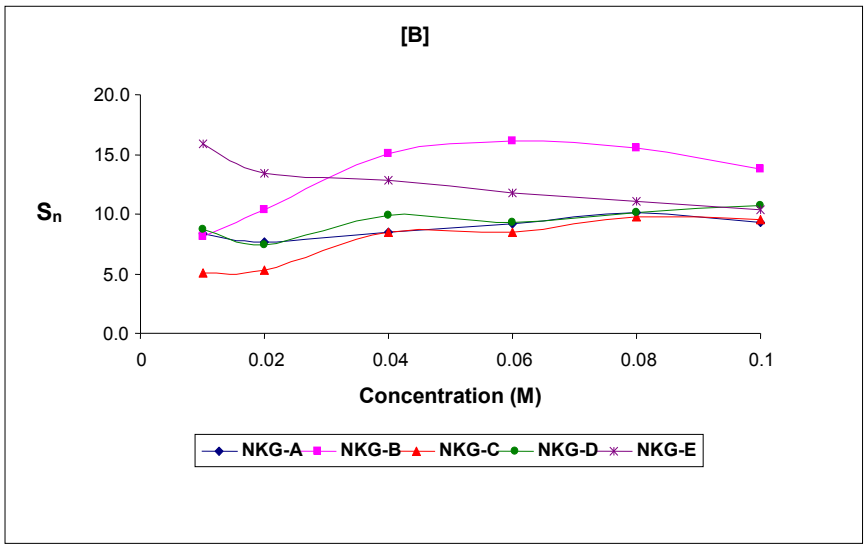


Figure 5. Variation of Solvation Number (S_n) with concentration of 1,5-benzodiazepine in (A) DMF and (B) THF at 298.15 K.

4. CONCLUSION

All the studied compounds exhibited solute-solvent interactions in DMF and THF solutions.

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