



INTERACTIONS OF DMSO WITH AQUEOUS SOLUTIONS OF AN ASSORTMENT OF DIHYDROFORMAZAN IN DIFFERENT CONCENTRATION AT 298.15 K

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Abstract

The ultrasonic velocity, density and viscosity at 298.15k have been measured in the interaction of 88% an assortment of DMSO with aqueous solutions of dihydroformazan in different concentration. The acoustical parameters such as adiabatic compressibility (β_s), intermolecular free length (Lf), relative association (RA) and Specific acoustic impedance (Zs), Viscous relaxation time (τ), apparent molar compressibility (Φ_k), limiting apparent molar compressibility (Φ^0_k), apparent molar volume (Φ_v), limiting apparent molar volume of solute (Φ^0_v) and solvation number (Sn) have been computed. Viscosity A, B coefficients have been obtained using the Jones-Dole equation. It is interesting to note that the DMSO molecules create structural effects in part.

Keywords: DMSO, Intramolecular, acoustic impedance.

1. Introduction

Ultrasonic analysis of biological specimens began at the end of the First World War. There were substantial works on tissue studies in recent past survey of literature reveals that there have been five broad division of bio-acoustical studies of which the present work deals with the characterization of the specimen using the sound velocity [1-4].

Literaturereview on acoustical parameters measurements shows that very little work has been carried out for dihydroformazan. Thus, in the present challenge, *acoustical speed*

technique has been used for the better understanding of molecular interactions in some selected compounds. Therefore, an assortment of dihydroformazanvia, N'(benzilidene)-3-(pyrid-4-yl) dihydroformazan (S1), N'(4-methoxy benzilidene)-3-(pyrid-4-yl) dihydroformazan (S2), N'(2-hydroxyl benzilidene)-3-(pyrid-4-yl) dihydroformazan (S3), N'[(3Z) -6- pyridin-4-yl-1,4 dihydro-1,2,4,5-tetrazin-3(2H)-ylidene] aniline (S8), 4-methyl-N-[(3Z)-6-pyridin-4-yl-1,4-dihydro-1,2,4,5-tetrazin-3(2H)-ylidene] aniline (S9), in 88% DMSO-Water at 298.15K, over the concentration range, (0.01 – 0.002) mol.kg⁻¹. From acoustical parameter like density(d), velocity (Us) and viscosity (η_s) measurements, adiabatic compressibility (β_s), intermolecular free length (Lf), relative association (RA) and Specific acoustic impedance (Zs), Viscous relaxation time (τ), apparent molar compressibility (Φ_k), limiting apparent molar compressibility (Φ^0_k), apparent molar volume (Φ_v), limiting apparent molar volume of solute (Φ^0_v) and solvation number (Sn) have been computed. Viscosity A, B coefficients have been obtained using the Jones-Dole equation. All these consequences are accessible and discussed below [5-7].

2. Materials and Methods

The solutes used in the present investigation were synthesized by standard method as reported by the earlier workers [8-9]. Solvents 88% DMF-Water and 88% DMSO-Water used was prepared using DMSO of analytical grade and double distilled water.

These chemicals were obtained from E. Merck. All solvents were used after purification by distillation. Densities, Viscosities were measured at 25°C (298K). The temperature was maintained by a thermostatically controlled water bath LTB-10.

The densities of the solutions has been measured at 25°C (298K) by the hydrostatic plunger method. A monopan digital balance of least count 0.0001 g was used to record change in plunger weight dipped in solutions. The viscosities were calibrated with doubly distilled water, 88% DMSO-Water. Care was taken to reduce evaporation during the measurements. A thoroughly cleaned and dried Ostwald viscometer filled with experimental liquid was placed vertically in a glass-fronted, well-stirred water bath. After thermal equilibrium was attained, the flow times of the liquid were recorded with an accurate stopwatch (± 0.01 s). The present value for the liquid agrees with the literature value within a deviation of the order of (0.01 poise). Ultrasonic velocity measurements were made by variable path single crystal interferometer (Mittal Enterprises, Model F-81) at 2 MHz with accuracy of ± 0.03 %.

3. Results and Discussion

Generally the value of adiabatic compressibility decreases with increase in concentration. Variation of adiabatic compressibility with concentration is shown in Table. The adiabatic compressibility is found to decrease with increase in concentration of solute in both the solvents and hence, follows the ideal behaviour. This decreasing trend may be due to aggregation of solvent molecules around solute supporting the strong solute – solvent interaction. The similar decrease in β_s with increase in the concentration of solute has been observed by earlier workers [10-13] which might be interpreted due to the increase in strength of interaction in the system with increasing concentration of solute in the solutions. And the value of ultrasonic velocity increases with increase in concentration. The increase in ultrasonic velocity with concentration is shown in Table. S. Baluja [14] also observed the increase in sound velocity of 1-H-benzimidazole and 2-methyl benzimidazole derivatives in methanol and chloroform solutions at 298.15 K over a wide

range of concentration. The increase in ultrasonic velocity with concentration suggests powerful solute – solvent interaction. The increase in ultrasonic velocity is of structure maker type [15].

The viscosity of a solvent or solution is a measure of cohesiveness or rigidity present between either ions or ion – solvent or solution. As density and viscosity of any solution or solvent are directly related to each other, measured values show similar trend. The viscosity increases linearly with concentration which may be due to solute – solvent interactions between the molecules. Similar behaviour has been observed by Subha and co-workers [16] in the study of effect of polymer and temperature on the critical micellar concentration. It denotes the magnitude of either the solute – solute interaction or the solute – solvent interaction or both of the system. The calculated values of free length are presented in Table. At a given composition, free length is found to decrease with the increase in concentration in both the solvents [17] indicating the small inter solute distance and significant molecular interactions. With increase in concentration; number of solute in a given volume increases, thereby decreasing the free length. According to Eyring and Kincard [18], intermolecular free length (L_f) is a predominant factor in solvation chemistry [19]. Therefore, the solute may be considered as structure promoters under the existing conditions. It denotes magnitude of the association between two species. This process is influenced by polarization [20-23] of the solvent species by solute or that of solute by solvent molecules. Relative association increases with increase in concentration in 88% DMSO – Water. Therefore, it can be concluded that solute – solute interaction overcomes the solute–solvent interaction in 88% DMSO–Water.

The viscous relaxation time (τ) increases with increase in concentration, indicating the presences of molecular interaction. Thus, it is suggested that the molecules get rearranged due to co – operative process [24-26]. When the sound wave travels through a solution, certain part of it travels through the medium and rest gets reflected by the ion i.e. restriction for the free flow of sound velocity by the ions. The

character that decreases this restriction / backward movement of sound waves is known as acoustic impedance. It is found to increase with change in concentration indicating the presence of bulkier solute due to solute – solvent / solvent – solvent interactions which restricts the free flow of sound waves. As apparent molar compressibility (Φ_k) depends on adiabatic compressibility which in turn depends on concentration; it can be said that apparent molar compressibility (Φ_k) is related to concentration. It represents the magnitude of ion–solvent interaction. From it, the parameters limiting molar compressibility (Φ^0_k) and the slope (S_k) were evaluated and are presented in table. In 88% DMSO – Water system; the slope (S_k) is large than limiting molar compressibility (Φ^0_k), indicating large solute – solute interactions than solute – solvent interactions.

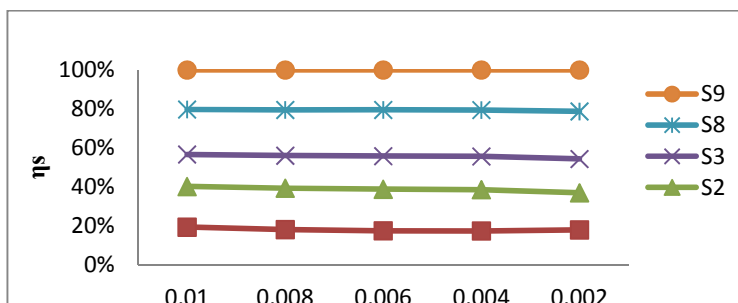
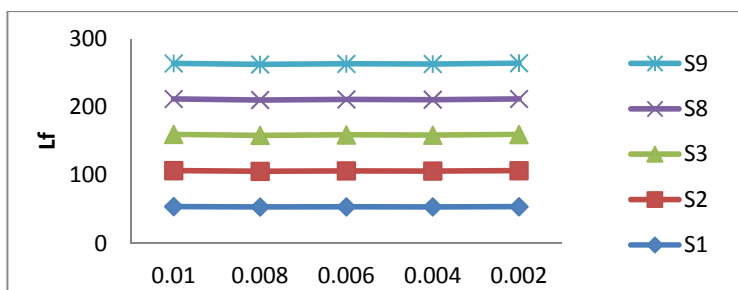
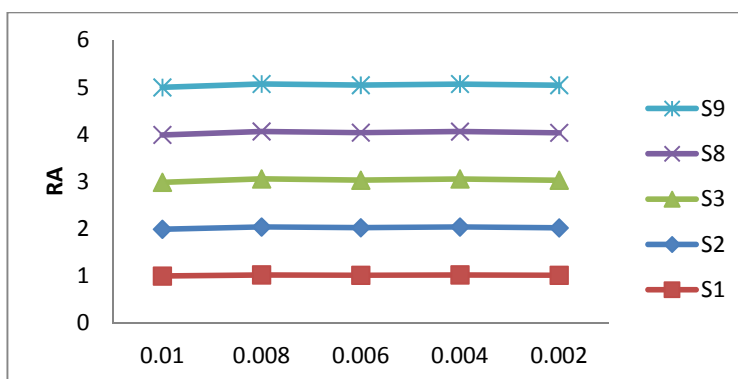
This is also further confirmed from variation of relative association (RA).

It is interesting to note that the DMSO molecules create structural effects in part because DMSO is a hydrogen bond acceptor but not donor, and in part because DMSO bonds with water. The solvated DMSO is likely bonded to two waters, which strengthens the attractive force between pairs of waters in the presence of DMSO [27-29]. A study of molecular association between water and DMSO in solution has been performed by Borin and Skaf [30] and observed the presence of DMSO-Water complexes at high DMSO concentrations. Due to this, the lone pairs of solvent are not much more available to solute for interaction, resulting in increase in solute-solute interaction in DMSO- water as compared to solute-solvent interactions.

Table I: Values Of Velocity (U_s), Viscosity (η_s), Adiabatic Compressibility (β_s), Intermolecular Free Length (L_f), Relative Association (RA), Viscous Relaxation Time (τ), Specific Acoustic Impedance (Z_s), Apparent Molar Compressibility (Φ_k), Apparent Molar Volume (Φ_v) And Solvation Number (S_n) For All Solutes In 88% DMSO-Water System At 298K.

Conc. (kg mol ⁻¹)	U_s (ms ⁻¹)	$\eta_s \times 10^3$ (Nsm ⁻²)	$\beta_s \times 10^{-10}$ (m ² N ⁻¹)	L_f (Å ⁰)	RA	$\tau \times 10^{-6}$ (s)	Z_s (kgm ⁻² s ⁻¹)	$\Phi_k \times 10^{-3}$ (m ² N ⁻¹)	Φ_v (m ³ mol ⁻¹)	$S_n \times 10^9$
S1										
0.01	1532.93	1.3222	7.99E-07	53.815	0.9982	1.41E-06	815.95	2.6E-05	489.686	-4056.53
0.008	1530	1.1941	7.84E-07	53.294	1.0223	1.25E-06	833.585	-0.0008	-335.53	131227.2
0.006	1529.2	1.13	7.92E-07	53.549	1.0138	1.19E-06	826.083	-0.0005	-185.62	85147.03
0.004	1527.3	1.115	7.88E-07	53.415	1.0219	1.17E-06	831.268	-0.0017	-1043.7	269432.7
0.002	1524.2	1.0965	7.98E-07	53.777	1.013	1.17E-06	821.78	-0.0011	-1169.6	180914.8
S2										
0.01	1560.93	1.4222	7.711E-07	52.85	0.9922	1.46E-06	830.853	-0.0008	489.686	124088.9
0.008	1557.3	1.4041	7.568E-07	52.359	1.0163	1.42E-06	848.459	-0.0018	-335.53	284781.7
0.006	1555.2	1.38	7.654E-	52.654	1.0082	1.41E-	840.128	-0.0018	-185.62	282357.2

			07			06					
0.004	1553.5	1.355	7.613E-07	52.514	1.0161	1.38E-06	845.528	-0.0036	-1043.7	566335.2	
0.002	1553.2	1.1651	7.688E-07	52.773	1.0066	1.19E-06	837.416	-0.0053	-1169.6	846642.4	
S3											
0.01	1552.93	1.1222	7.7903E-07	53.121	0.9938	1.17E-06	826.595	-0.0005	489.685	88182.3	
0.008	1550	1.1041	7.6397E-07	52.605	1.0179	1.12E-06	844.481	-0.0015	-335.52	244514.9	
0.006	1549.2	1.1	7.713E-07	52.857	1.0094	1.13E-06	836.887	-0.0015	-185.61	237727.1	
0.004	1548.3	1.095	7.6643E-07	52.690	1.0172	1.12E-06	842.697	-	0.00321	-1043.6	508604.8
0.002	1543.2	1.0651	7.7883E-07	52.091	1.0154	1.6331	822.754	-4.491	-1805.4	621316.4	
S8											
0.01	1576.66	1.5745	7.43E-07	51.874	1.0060	1.56E-06	853.789	-0.002	-2.731	257051	
0.008	1574.6	1.5506	7.45E-07	51.943	1.0063	1.54E-06	852.636	-0.002	-113.4	324126	
0.006	1573.73	1.5326	7.46E-07	51.983	1.0061	1.52E-06	851.782	-0.003	-278.5	439605	
0.004	1573	1.5239	7.47E-07	52.007	1.0062	1.52E-06	851.386	-0.004	-640.8	679891	
0.002	1570.93	1.4923	7.49E-07	52.078	1.0066	1.49E-06	850.192	-0.009	-1716	1E+06	
S9											
0.01	1569.33	1.386	7.51E-07	52.141	1.0065	1.39E-06	848.996	-0.001	25.256	218862	
0.008	1568.93	1.3549	7.51E-07	52.151	1.0068	1.36E-06	848.893	-0.002	-84.84	286754	
0.006	1566.6	1.3255	7.53E-07	52.242	1.0067	1.33E-06	847.182	-0.002	-236.4	378188	
0.004	1565.6	1.3188	7.54E-07	52.276	1.0069	1.33E-06	846.642	-0.004	-577.9	584753	
0.002	1560.93	1.3017	7.59E-07	52.440	1.0077	1.32E-06	843.879	-0.007	-1562	1E+06	

Fig.1 Plot of Viscosity (η_s) of solution against molality(m)**Fig.2 Plot of Free length (Lf) of solution against molality(m)****Fig.1 Plot of Relative association (RA) of solution against molality(m)**

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