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Effect of solvents on acoustic properties of dihydroformazan and 1,2,4,5 – tetrazins at 10°C.

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Abstract: In the present attempt, ultrasonic technique has been used for the better understanding of molecular interactions in some selected dihydroformazan and 1,2,4,5 – tetrazins. From density, velocity (U_s) and viscosity (η_s) measurements, adiabatic compressibility (β_s), intermolecular free length (L_f), relative association (RA) and Specific acoustic impedance (Z_s), Viscous relaxation time (τ), apparent molar compressibility (Φ^0_k), limiting apparent molar compressibility (Φ^0_k), apparent molar volume (Φ^0_v), limiting apparent molar volume of solute (Φ^0_v) and solvation number (Sn) have been computed. It is interesting to note that the DMSO molecules create structural effects in part.

I. Introduction

Ultrasound velocity along with related thermo acoustic parameters has been extensively used in the recent years to study molecular interaction in binary and ternary liquid mixtures by number of researchers^[1-6]. Over many years, studies of thermodynamic and transport properties of model compounds such as alkali halide, tetra-alkyl ammonium halides, hydrocarbons, alcohols and amines have witnessed the importance of solute-solvent interactions^[7-13].

Literature survey on ultrasound velocity measurements shows that very little work has been carried out for dihydroformazan and 1,2,4,5 – tetrazins. Thus, in the present attempt, this technique has been used for the better understanding of molecular interactions in some selected compounds. Therefore, it was thought worthwhile to undertake thermodynamic and acoustic studies of the solutes via, 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' (4-dimethyl benzilidene)-3-(pyrid-4-yl) dihydroformazan (S4), N' (3-nitro benzilidene)-3-(pyrid-4-yl) dihydroformazan (S7), 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 different solvents like 85% DMF–Water and 85% DMSO–Water at 285K, over the concentration range, (0.01 – 0.002) mol.kg⁻¹. From density, velocity (U_s) and viscosity (η_s) measurements, adiabatic compressibility (β_s), intermolecular free length (L_f), relative association (RA) and Specific acoustic impedance (Z_s), Viscous relaxation time (τ), apparent molar compressibility (Φ^0_k), limiting apparent molar compressibility (Φ^0_k), apparent molar volume (Φ^0_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 results are presented and discussed below.

II. Materials and Methods

The solutes used in the present investigation were synthesized by standard method as reported by the earlier workers^[14]. Solvents 85% DMF-Water and 85% DMSO-Water used were prepared using DMF, 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 10°C (283K). The temperature was maintained by a thermostatically controlled water bath LTB-10.

The densities of the solutions has been measured at 10°C (283K) 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, 85% DMF-Water and 85% 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 ($\pm 0.01s$). 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 %.

III. Results and Discussion

Ultrasonic velocity (U): Generally the value of ultrasonic velocity increases with increase in concentration. The increase in ultrasonic velocity with concentration is shown in Table III. S. Baluja^[15] 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^[16].

Viscosity (η): 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^[17] in the study of effect of polymer and temperature on the critical micellar concentration.

Adiabatic compressibility (β_s): Generally the value of adiabatic compressibility decreases with increase in concentration. Variation of adiabatic compressibility with concentration is shown in Table III. 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^[18-19] which might be interpreted due to the increase in strength of interaction in the system with increasing concentration of solute in the solutions.

Intermolecular free length (L_f): 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 III. At a given composition, free length is found to decrease with the increase in concentration in both the solvents^[20] 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^[21], intermolecular free length (L_f) is a predominant factor in solvation chemistry^[22]. Therefore, the solute may be considered as structure promoters under the existing conditions.

Relative association (RA): It denotes magnitude of the association between two species. This process is influenced by polarization^[23] of the solvent species by solute or that of solute by solvent molecules. Relative association increases with increase in concentration in 85% DMSO – Water. Therefore, it can be concluded that solute – solute interaction overcomes the solute–solvent interaction in 85% DMSO–Water. But in 85% DMF–Water, solute–solvent interaction plays the role. A similar increase in the value of RA has been found in case of sucrose solution in water + AN mixtures^[24], however, in 85% DMF–Water, there is decrease in RA value with increase of solute concentration^[25].

Viscous relaxation time (τ): 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^[26].

Specific acoustic impedance (Z_s): When the sound wave travels through a solution, certain part of it travels through the medium and rest gets reflected by the ion^[27-28] 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.

Apparent molar compressibility (Φ_k): 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 IV. In 85% DMF – Water system; limiting molar compressibility (Φ^0_k) appears to be larger than the slope (S_k) indicating predominance of solute – solvent interaction over solute – solute interaction^[29].

In 85% 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). Here again S_7 shows different behaviour than other molecules, which may be due to changes in local compressibility of solvent.

Solute – solute (A) and solute – solvent (B) interaction: Above interaction is confirmed from the values of solute–solute (A) and solute–solvent interactions (B) as listed in table 2. The values of A are lower in 85% DMF–water than 85% DMSO–water, favouring solute–solute interaction^[30] in 85% DMSO–Water; whereas the B–value shows irregular trend which may be due to simultaneous solute–solute and solute–solvent interactions.

Apparent molar volume (Φ_v): Apparent molar volume (Φ_v) is defined as the change in volume of the solution for the added concentration at a constant temperature and pressure. The limiting molar volume (Φ^0_v) and the experimental slope (S_v) are evaluated and listed in Table 1. These values show same behaviour as that of limiting molar volume (Φ^0_v) and the experimental slope (S_v) which support to our findings.

Solvation Number (Sn):- It is the number of solvent molecules associated and taking part in the formation of primary shell with the central ion^[31]. But, as the study restricts to solute particles, not the ions; so, no clear idea can be drawn about solvation number. There is again irregularity in solvation number confirming the dynamic equilibrium.

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^[32]. A study of molecular association between water and DMSO in solution has been performed by Borin and Skaf^[33] and observed the presence of 2DMSO·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 interaction in all solutes except S7.

With water, DMF forms C-H---O type hydrogen bond interactions resulting in the complex H-bonded network structure of this system. The typical geometry of water pairs, characteristic of pure water, is partially maintained in the mixtures^[34]. On the other hand, both the average number of water-water H bonds and the total H bonds per water molecule decrease with increasing DMF concentration. Hence, it can readily interact with solutes through lone pairs, giving rise to large solute-solvent interaction in DMF- water as compared to solute-solute interaction in all solutes except S7.

In all the solutes, the substituent is present at ortho/ para positions (electron donating group) activating the benzene ring but in S7, presence of –NO₂ group at m-position (electron withdrawing group) deactivates the benzene ring which might be the reason for its abnormal behavior.

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