A study of substituded dihydroformazan in predicting the acoustical and its allied properties in different solvents at 288.15K

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ABSTRACT

Densities, speed of sound and viscosity were measured for substituted dihydroformazan in different solvents like 88% DMF-water and 88% DMSO-water medium at 288.15K. A quantitative relationship has been established among the thermodynamic properties like acoustical impedance, sound velocity, internal pressure, adiabatic compressibility, intermolecular free length, apparent molar compressibility, apparent molar volume etc. The results obtained are very much comparable and in good agreement. A molecular interaction study has also been made successfully in the light of these acoustical properties.

Keywords: dihydroformazans, ultrasonic velocity, apparent molar volume, acoustical impedance.

INTRODUCTION

Dihydroformazan and 1,2,4,5-tetrazins are the class of compounds which are found to contain antimicrobial, antimicrobacterial activity, antiviral activities against various virus, bacteria and fungi strains. So, it was found important to study their ultrasonic and thermodynamic behavior which may lead to some new findings in future. Ultrasonic can be viable technology because it is readily available and can be used for wide range of application in fields like consumer industries, pharmaceutical, medical field process industries, chemical industries and physics etc [1-3]. In chemistry, ultrasound velocity along with related thermo acoustic parameters have been extensively used in the recent years to study molecular interaction in binary and ternary liquid mixtures by number of researchers [4-6]. 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 showed that very little work has been carried out for dihydroformazan. Thus, in the present paper we have used this technique for the better understanding of molecular interactions in these compounds. Therefore, it was thought worthwhile to undertake thermodynamic and acoustic studies of the compounds via, N'

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(benzilidene) – 3 – (pyrid – 4 – yl) dihydroformazan (S1) in different solvents 88% DMF – Water and 88% DMSO - Water. We report here, densities, relative viscosities of (S1 + 88% DMF - Water), (S1 + 88% DMSO - Water) at 288K, over the concentration range, (0.01 – 0.002) mol.kg-1. From density measurements, apparent molar compressibility (Φk), limiting apparent molar compressibility (Φ^0k),the apparent molar volume (Φv), limiting apparent molar volume of solute (Φ^0v), molar compressibility (W), relaxation strength (r), salvation number (Sn), specific volume (V) and internal pressure (π) have been computed and using density and viscosity data, the Jones-Dole equation viscosity A, B coefficients have been obtained. The results of all these presented and discussed below.

MATERIALS AND METHODS

The solutes used in the present investigation were synthesized by standard method as reported by the earlier researchers [14]. Solvent DMF and DMSO used were of analytical grade. They were obtained from E. Merck chemical company. All solvents were used after purification by distillation. Densities, Viscosities were measured at 288 K. The temperature was maintained by a thermostatically controlled water bath LTB-10.

The densities of the solutions were measured at five different temperatures 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 with DMF and DMSO. 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 stability was attained, the flow times of the liquid were recorded with an accurate stopwatch correct to (0.01s).The present value for the liquids agree 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-81S) at 2 MHz with accuracy of $\pm$ 0.03 %.

3. Theory and calculation
The relative viscosities have been analysed by Jones-Dole equation [15].

$$(\eta_r - 1) / \sqrt{c} = A + B \sqrt{c} \qquad\qquad\qquad ………. (1)$$

where, c is molar concentration of the ligand solution, A is the Falkenhagen coefficient which is the measure of solute – solute interactions and B is the Jones-Dole coefficient which is the measure of solute - solvent interaction.

The apparent molal volumes (ϕv) and apparent molal adiabatic compressibilities (ϕk$_{(s)}$) in solutions are determined respectively, from density (ds) and adiabatic compressibility (βs) of solution using the equation,

$$\phi v = (M/ds) + [(do – ds)10^3] / m \, ds \, do \qquad\qquad … … … (2)$$

and $\qquad$ ϕk$_{(s)}$ = [1000 (βs do – βo ds) / m ds do] + (βs M /ds) $\qquad$ …… (3)

where, do is the density of pure solvent, m is molality, M is the molecular weight of solute, βo is adiabatic compressibility of pure solvent and βs is adiabatic compressibility of solution.

βs is calculated from ultrasonic velocity using the equation –

$$\beta s = 100 / (U s^2 ds) \quad \dots (3a) \quad \text{and} \quad \beta o = 100 / U o^2\, do \quad \dots (3b)$$

where, $U s$ is the ultrasonic velocity in the solution in m/s. βs is in bar^{-1} and $\phi k_{(s)}$ is in $cm^3\, mol^{-1}\, bar^{-1}$. The values of $\phi k_{(s)}$ and ϕv were plotted versus $\sqrt{\text{molality}}$ of solutes. The curves represent the least square and ϕv can be given as–

$$\phi v = \phi^0 v + S v \sqrt{m} \quad \dots \dots \dots (4) \text{ and } \phi k_{(s)} = \phi^0 k_{(s)} + S k_{(s)} \sqrt{m} \quad \dots \dots \dots (5)$$

where, $\phi^0 v = v^0$ and $\phi^0 k_{(s)} = k^0$ are the infinite dilution apparent molal volumes and apparent molal adiabatic compressibilities respectively. $S v$ and $S k_{(s)}$ are the experimental slopes representing ion-ion interactions.

The intermolecular free length (Lf), specific acoustic impedance (z) and relative association (RA) [16] are calculated by using the following equation-

$$Lf = K \times \sqrt{\beta s} \qquad \dots \dots \dots (6)$$
$$Z = U s \times ds \qquad \dots \dots \dots (7)$$
$$R_A = \frac{ds}{do} \left| \frac{Uo}{Us} \right|^{1/3} \qquad \dots \dots \dots (8)$$

From the graph of $\phi k(s)$ versus $\sqrt{m}$, $\phi^0 k(s)$ (thermodynamic parameter i.e., limiting molal adiabatic compressibility) at zero mole fraction have been evaluated, as given in table 2.
Viscous relaxation time τ was calculated using the equation;

$$\tau = 4\eta / 3\, ds \times U s^2 \qquad \dots \dots \dots (9)$$

Molar compressibility W was calculated using the equation;

$$W = M \times (\beta s)^{-1/7} / ds \qquad \dots \dots \dots (10)$$

The relaxation strength (r) was calculated using the equation;

$$r = 1 - (U s / U\alpha)^2 \qquad \dots \dots \dots (11)$$

where, $U\alpha = 1600\ ms^{-1}$

The solvation number (Sn) [16] was calculated using the equation;

$$Sn = - (\phi k_{(s)} / \beta o \times M\ \text{solute} \times do) \qquad \dots \dots \dots (12)$$

Values of specific volume (V = 1/ ds) was also reported in the table and the internal pressure (Π) was calculated by the equation given by Pandey [17],

$$\Pi = 44.2 \times T^{4/3} \times U s^{3/2} \times ds \qquad \dots \dots \dots (13)$$

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Table I :- Variation of ultrasonic velocity (Us), relative viscosity (ηs), adiabatic compressibility(βs), intermolecular free length (Lf), relative association (RA), viscous relaxation time (τ) and specific acoustic impedance (Zs) with different concentration and different solvents - 88% DMF – Water and 88% DMSO – Water on 15⁰C (288.15K)

Conc. (kg mol^{-1})	Us cms^{-1}	Hs cp	Bs Cm^{2}dyn^{-1}	Lf A^0	RA	τ s	Zs g/s.cm^2
S1 - 88% DMF – Water							
0.01	1602.4	0.851242	7.952E-07	53.67239	1.004846	9.026E-07	785.70677
0.008	1595.86	0.832935	7.992E-07	53.80574	1.005051	8.875E-07	783.55045
0.006	1594.4	0.791618	8.018E-07	53.89304	1.005408	8.463E-07	782.21901
0.004	1586.4	0.777326	8.104E-07	54.18088	1.006498	8.399E-07	777.83254
0.002	1582.93	0.754136	8.140E-07	54.30216	1.00714	8.185E-07	776.05960
S1 - 88% DMSO – Water							
0.01	1633.86	1.607659	7.3263E-07	51.51557	1.017865	1.570E-06	835.409
0.008	1619.33	1.56143	7.5063E-07	52.14467	1.014378	1.562E-06	822.6893
0.006	1614	1.508639	7.5652E-07	52.34887	1.014252	1.521E-06	818.9791
0.004	1610.93	1.491985	7.5997E-07	52.46823	1.014138	1.511E-06	816.8108
0.002	1600	1.437383	7.7224E-07	52.8898	1.014016	1.48E-06	809.3328

Table II :- Apparent molar compressibility (Φk), apparent molar volume (Φv), molar compressibility (W), relaxation strength (r), salvation number (Sn), specific volume (V) and internal pressure (π) at 88% DMF – Water and 88% DMSO – Water on 10⁰C (288K).

Conc. Molal	Φk(s) Cm^{2}dyn^{-1}mol^{-1}	Φv cm^{3}mol^{-1}	W	R	Sn	V	Π atm
S1 - 88% DMF – Water							
0.01	0.000271	381.7743	3604.961	-0.0005	-39606.09	2.036892	9.5089E+19
0.008	0.000373	371.4974	3604.33	0.003921	-54463.17	2.03798	9.4409E+19
0.006	0.000476	339.3797	3603.233	0.006988	-69568.42	2.038304	9.3959E+19
0.004	0.001062	301.1723	3599.889	0.016928	-155073.9	2.039514	9.2497E+19
0.002	0.002179	126.4777	3597.922	0.021224	-318146.9	2.039702	9.1883E+19
S1 - 88% DMSO –Water							
0.01	-0.00087	-66.2843	3502.172	-0.04277	135062.9	1.955761	1.0537E+20
0.008	-0.00046	-59.9156	3512.491	-0.02431	70904.99	1.968337	1.0193E+20
0.006	-0.00042	-71.5727	3512.865	-0.01758	65206.8	1.970746	1.0080E+20
0.004	-0.00063	-392.55	3513.204	-0.01371	98114.91	1.972219	1.0015E+20
0.002	0.000215	-863.005	3513.565	0	-33525	1.976937	9.7900E+19

Table III :- Values of A, B, Φ⁰v, Sv, Φ⁰k(s), Sk(s) for N' (benzilidene) – 3 – (pyrid – 4 – yl) dihydroformazan (S1) with different solvents 88% DMF – Water 88% and DMSO – Water at 15⁰C(288K)

Compound (S1)	A	B	Φ^{0}v cm^{3}mol^{-1}	Sv (cm^{3}mol$^{-3/2}$dm$^{1/2}$)	Φ^{0}k(s) Cm^{2}dyn^{-1}mol^{-1}	Sk(s) cm^{3}dyn^{-1}mol$^{-3/2}$ dm$^{1/2}$
88% DMF – Water	0.667241	0.790093	-28.9254	4441.358	0.003444	-0.03431
88% DMSO – Water	1.300095	1.952024	-1422.329	15260.995	0.000695	-0.015027

RESULTS AND DISCUSSION

Density (d) is a measure of solvent – solvent and ion – solvent interactions. Increase in density with concentration indicates the increase in solvent – solvent and solute – solvent interactions, whereas decrease in density indicates lesser magnitude of solvent – solvent and solute – solvent interactions.

Viscosity (η) in association with density provides useful information in regard to different types of interactions involved in the ionic solutions [18]. Several groups [17] have utilized density and

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viscosity data to deduce the thermodynamic properties of electrolytic solutions. Viscosity of a solvent or solution is a measure of cohesiveness or rigidity present in between either ions or ion – solvent or solvent – solvent molecules present in a solution or solution.

Ultrasonic velocity (U) depends on the wavelength λ of the sound wave. Since the frequency F is a constant. Λ increased with the increase in concentration. So also U increase with the increase in concentration of S1 with 88% - DMF – Water and 88% - DMSO – Water.

Adiabatic compressibility (β) when an ion is added to a solvent, It attract certain solvent molecules towards itself by wrenching the molecule species from the bulk of the solvent. Hence less number of solvent molecules will be made available for the next incoming species. This is known as compression. Every solvent has a limit for compression and is known as limiting compressibility. Generally the value of β_{ad} decrease with increase in concentration while Z increases [18].

Acoustic impedance (Z) is the product of ultrasonic velocity and density. Intermolecular free length (Lf) depends on the intermolecular attractive and repulsive forces. The attractive force depends on the distance between the centers of attraction of the molecules, whereas the repulsive force depends on the distance between the surfaces of the molecule.

Relative association (R_A) is decrease in relative association R_A may be due to the breaking up of the solvent molecules on adding the solute, whereas the increase in R_A may be due to the salvation of solute [19]. Solvation Number (Sn) is the number of solvent molecules attached to the central ion by surrounding their translational degree of freedom.

It has been observed from table I – that, in DMSO – Water solvent; viscosity is increase and adiabatic compressibity decreases. This shows that molecules are closer in DMSO than DMF. This also reflects in decrease in the value of intermolecular free length. As a result of which relative association increases, solute practical get associated more in DMSO , This can be due to inter atom of lone pair of both S and O with the H and lone pair of N present in solute.

The large and small values of 'A' show the stronger and weaker solute – solute interactions respectively. When the solute is introduced into solvent of organic-water mixture, it will interfere with the ordered structure of water in the solute's co sphere. As only one solute is present, so such variation in the values of A can be explained. It is evident from Table 2 that the B-coefficient is an adjustable parameter, which may be either positive or negative and it is a measure of the effective hydrodynamic volume of solute which accounts for the solute-solvent interactions. It is known as a measure of order or disorder introduced by the solute into the solvent. Solutes with negative viscosity B-coefficient is characterized as "Structure breakers" indicating weak solute-solvent interactions. Such types of results are also shown by Eyring [20]. The same also results in less value of Φk, Φv, RA and V in DMSO – Water solvent. Solute – solute (A) as well as solute – solvent (B) interaction is more in DMSO solvent.

Water is also present in solvent. The H – bonding tendency of water binds lone pair of N in DMF and lone pair of sulfur/oxygen in DMSO. But still in DMSO, more number of lone pairs are available for interaction with solute, while in case of DMF, solute – solvent interaction decreases, as only lone pair of N are available for such interaction.

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