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Adiabatic compressibility, apparent molal volume, apparent molal compressibility and solvation number of substituted 2-oxo-2-H-chromene-3-carbohydrazide derivatives in 70% DMF-Water

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ABSTRACT

Ultrasonic study of substituted 2-oxo-2-H-chromene-3-carbohydrazide derivatives in 70% DMF-water at 305K is done. The experimental data is used to calculate adiabatic compressibility, apparent molal volume, apparent molal compressibility and solvation number. These acoustic parameters are used to explain the interaction taking place in the solutions.

Keywords: Substituted 2-oxo-2-H-chromene-3-carbohydrazide derivatives, acoustic parameters and interactions in solutions.

INTRODUCTION

Ultrasonic study has wide range of application in material science, agriculture, medicine, biology, industry, oceanography, sonochemistry research due to its non-destructive nature[1-2]. The ultrasonic velocity measurement is used to provide qualitative information about the physical nature and strength of molecular interaction in the liquid mixture[3]. Ultrasonic technique is applied to impart positive effects in food processing such as improvement in mass transfer, food preservation, assistance of thermal treatments and manipulation of texture and food analysis[4].Ultrasonic technique is utilized for measuring the thickness of skin and biological tissues[5]. The determination of ultrasonic properties of pure solvents and their solutions finds wide range of applications in chemical, pharmaceutical, polymer and bio-chemical industries[6]. Ultrasonic technique is used to determine antimicrobial activity of schiff bases[7]. Anti-inflammatory property of phenylalanine analogus as schiff bases is reported[8].Ultrasonic velocity finds extensive application in solution theory and molecular dynamics[9].Ultrasound velocity along with related thermo acoustic parameters have extensively used in the recent years to study molecular interaction in binary and ternary liquid mixtures by number of researchers[10-12].

Acoustic characteristics have studied for sodium salt of N-chloro-p-toluene sulphonamide in aqueous and binary aqueous media [13]. Adiabatic compressibility, apparent molal volume, apparent molal compressibility and solvation number of substituted azomethine drugs are reported[14]. The physico-chemical behavior for pure liquid components and their mixtures is studied on the basis of acoustic and thermodynamic properties[15]. Ultrasonic velocity and density have measured for non- aqueous solution of the ligands in DMSO solvent at 306K [16]. The acoustical properties of 1-(2'-hydroxy-5' bromophenyl)-3-(4'-chlorophenyl)-1, 3 pronandione in dioxane-water mixture and also in different percentage of dioxane are reported[17].The ultrasonic velocity measurements of substituted hydrazone in 70% (DMF+water) solvents in different concentration is studied[18].Ultrasonic study is carried out for substituted 2, 3-dihydroquinazolin-4(1*H*)-ones in 70% DMF-Water at temperature 303K[19]. Molecular interaction of amide with aliphatic amine in benzene at different temperatures is reported[20]. Ultrasonic velocity and density measurements are done for levofloxacin, hemihydrate, tacrolimus, monohydrate and

lisinoprildihydrate at two different temperatures[21]. Acoustic parameters of binary mixtures of toluene with heptan-1-ol, octan-1-ol and decan-1-ol have calculated over the entire range of composition, different temperature (298.15 and 308.15K) and at atmospheric pressure[22]. Ultrasonic technique is used to determine intermolecular interaction of 2-chlorobenzaldehyde[23]. The study of apparent molal volumes of alcohols in aqueous solutions at different temperatures is carried out[24]. The study of molecular interaction and physico-chemical behavior of zwitter-ionic nature of amino acids in water is done[25-26]. Ultrasonic velocity and density measurements are carried out for 3-(Chloroaryl)-5-aryl-1-Pyrazolines at different percentage of dioxane as solvent for investigating solute-solvent, solute-solute interaction at different temperature[27]. The molecular interaction and physico-chemical behavior of some divalent transition metal sulphates in aqueous propylene glycol at 303.15K have studied by using ultrasonic technique[28]. Molecular interactions of substituted N, N'bis(salicyliden)-arylmethanediamines in binary mixture of DMF-Water are very well studied by the different acoustic parameters, which helps to understand that there is weak solute-solvent interaction[29]. Apparant molar volume of NaCl has studied in dioxane, glycol, ethanol, propane-2-ol, methanol, glycerol-water mixture at 10, 20 and 30% (W/W) within the temperature range 303-313K[30]. Isentropic compressibillities are reported for binary mixtures of 1, 2-ethane diol with 1-hexanol, 1-butanol, or 1-octanol in the temperature range 293.15-313.15K[31]. Ultrasonic velocity and density of substituted aminopyrimidine in 70% DMF solvent are measured at 300K and different concentration[32].

In the present work, different properties such as adiabatic compressibility (β_s), apparent molal volume (ϕ_v), apparent molal compressibility (ϕ_k) and salvation number (S_n) have been evaluated in following substituted-2-oxo-2-H-chromene-3-carbohydrazide derivatives in 70% (DMF+Water) mixture at different concentrations of ligand at 305K.

Ligand (L_A) = N-[(E)-1-(5-bromo-2-hydroxy-phenyl)ethylideneamino]-2-oxo-chromene-3-carboxamide
Ligand (L_B) = N-[(E)-1-(5-chloro-2-hydroxy-phenyl)ethylideneamino]-2-oxo-chromene-3-carboxamide
Ligand(L_C) = N-[(E)-1-(3,5-dichloro-2-hydroxy-phenyl)ethylideneamino]-2-oxo-chromene-3-carboxamide
Ligand (L_D) = N-[(E)-1-(2-hydroxy-5-methyl-phenyl)ethylideneamino]-2-oxo-chromene-3-carboxamide

MATERIALS AND METHODS

All the chemicals used are of A R grade. The density measurements are done with the precalibrated bicapillary pyknometer. All the weighings are done on one pan digital balance (petit balance AD-50B) having an accuracy of $\pm$ 0.001 gm. The speed of sound wave is obtained by using variable path crystal interferrometer (Mittal Enterprises, Model MX-3) with accuracy of $\pm$ 0.03% and frequency 1MHz. In the present work, a steel cell fitted with a quartz crystal of variable frequency is employed. The instrument is calibrated by measuring ultrasonic velocity of water at 32^o C.

RESULTS AND DISCUSSION

The ultrasonic waves of known frequency produced by a quartz crystal are reflected by a movable metallic plate kept parallel to the quartz plate. When the state of acoustic resonance is reached due to the formation of standing waves, an electrical reaction occurs on the generator driving the quartz plate and its anode current becomes maximum. The micrometer is slowly moved until the anode current meter on a high frequency generator shows a maximum. The distance thus moved by the micrometer gives the values of wavelength[33].

The distance traveled by micrometer screw to get one maximum in ammeter (D) is used to calculate wavelength of ultrasonic wave using following relation:

$$2D = \lambda \quad (1)$$

Where, λ is wavelength and D is distance in mm.

From the knowledge of the wavelength, the ultrasonic velocity can be obtained by the relation:

$$\text{Ultrasonic velocity (U)} = \lambda \times \text{Frequency} \times 10^3 \quad (2)$$

Using the measured data some acoustical parameters can be calculated using the standard relations.

The adiabatic compressibility[34] of solvent and solution can be calculated by using equations:

$$\text{Adiabatic compressibility of solution } (\beta s) = 1/ Us^2 \times ds \quad (3)$$

$$\text{Adiabatic compressibility of solvent } (\beta_0) = 1/ U_0^2 \times d_0 \quad (4)$$

Where, U_o and Us are ultrasonic velocity in solvent and solution respectively.

d_o and ds are density of solvent and solution respectively.

The apparent molal volume (ϕ_v) and apparent molal compressibility (ϕ_k) are given by following equations[35].

$$\text{Apparent molal volume } (\phi_v) = \frac{M}{d_s} + \frac{(d_o - d_s)\times 10^3}{(md_s d_0)} \quad (5)$$

$$\text{Apparent molal compressibility } (\phi_k) = \frac{1000(\beta_s d_o - \beta_o d_s)}{md_s d_o} + \frac{\beta_s M}{d_s} \quad (6)$$

Where, d_o and d_s are the densities of the pure solvent and solution, respectively.

m is the molality and M is the molecular weight of solute.

β_o and β_s are the adiabatic compressibility of pure solvent and solution respectively.

The solvation number (S_n)[36] is given by the equation.

$$\text{Solvation number } (S_n) = \phi_k / \beta_0 \text{ x } (M/ d_0) \quad (7)$$

In present work the measurement of ultrasonic velocity and density at a different concentration of substituted 2-oxo-2-H-chromene-3-carbohydrazide derivatives in 70% DMF+water solvent is carried out at 305K temperature. The data obtained is used to determine adiabatic compressibility (β_s), apparent molal volume (ϕ_v), apparent molal compressibility (ϕ_k) and solvation number (S_n) of substituted 2-oxo-2-H-chromene-3-carbohydrazide derivatives using equations 3, 5, 6 and 7. From table no. 1 it is observed that ultrasonic velocity decreases with decreases in concentration in the system. This is due to association of very strong dipole-induce dipole interaction between the components. In more concentrated solution the possibility of making hydrogen bond increases which gives packed structure due to this ultrasonic velocity increases.

The compressibility gives the ease with which a medium can be compressed. Table no. 1 show that the adiabatic compressibility (β_s) increases with decrease in the concentrations. Fig. no. 2 shows the variation of adiabatic compressibility with concentrations. In more concentrated solution more cohesion is expected and this lead to a decrease in adiabatic compressibility (β_s). The decrease in adiabatic compressibility (β_s) results in an increase in the value of ultrasonic velocity. The increase of adiabatic compressibility with decrease of concentration of solution due to the dispersion of solvent molecules around ions supporting weak ion solvent interactions.

Apparent molal volume (ϕ_v) is very important tool to identify ion-solvent interactions. Table no.1 suggests that the apparent molal volume (ϕ_v) increases with decrease in concentration in all the system. Fig. no. 3 shows the variation of apparent molal volume with concentrations. The increase in apparent molal volume with decrease in concentration in all systems indicates the existence of strong ion-solvent interaction.

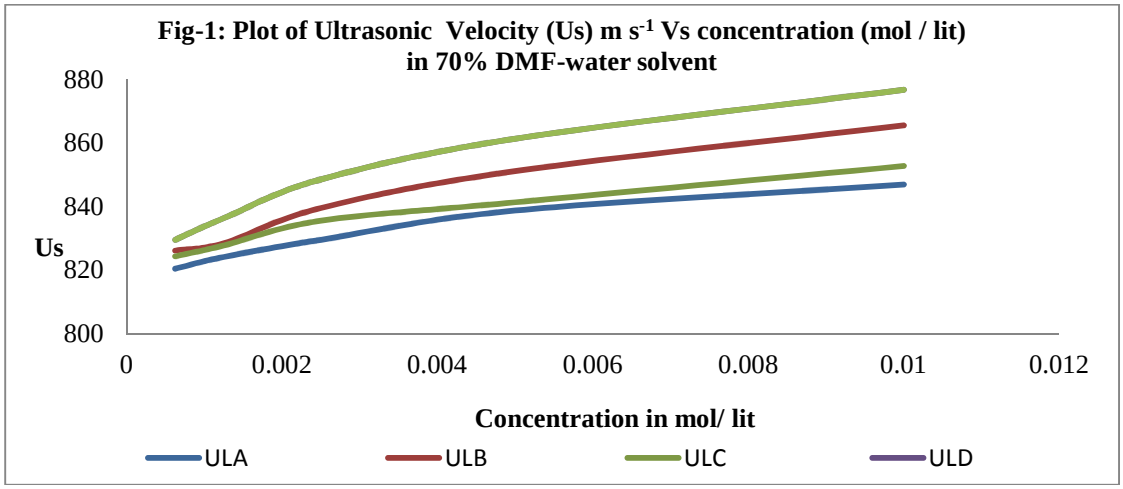
Table no. 1 shows the variation of apparent molal compressibility (ϕ_k) with concentrations. Fig. no. 4 suggests that apparent molal compressibility (ϕ_k) increases with decreases in concentrations. The increase in value of apparent molal compressibility (ϕ_k) with decrease in concentrations in this systems, shows the weak electrostatic attractive force in the vicinity of ions causing electrostatic salvation of ions.

The solvation number (Sn) increases as the concentration decrease as per table no. 1. Fig. no. 5 shows the variation of solvation number with concentrations. When salvation occurs, the solvent molecules of the ion-solvent complex may be assumed to more closely pack than in the pure solvent. The increase in solvation number with decrease in concentration is due to weak solute-solvent interaction in this system.

Table 1: Density (d), ultrasonic velocity (U_s), adiabatic compressibility (β_s), apparent molal volume (ϕ_v), apparent molal compressibility (ϕ_k) and solvation number (S_n) in 70% DMF solvent at 305K

Conc. (m) (mol lit^{-1})	Density (d) (kg m^{-3})	Ultrasonic Velocity (U_s) (m s^{-1})	Adiabatic compressibility (β_S) x 10^{-9}, (m^{2}N^{-1})	Apparent molal volume (ϕ_v) (m^{3}mol^{-1})	Apparent molal compressibility (ϕ_k) x 10^{-10} (m^{2}N^{-1})	Solvation number (S_n)
Ligand L_A						
0.01	1227.2	847.0	1.1358	7.5529	4.8080	0.6113
0.005	1221.4	838.8	1.1637	15.0171	5.0611	0.6457
0.0025	1218.6	829.6	1.1923	29.9192	5.1899	0.6622
0.00125	1215.9	824.2	1.2107	59.4901	5.3011	0.6763
0.000625	1214.1	820.5	1.2235	118.5120	5.4200	0.6915
Ligand L_B						
0.01	1168.8	865.6	1.1419	5.8377	4.0319	0.5802
0.005	1166.1	851.2	1.1836	11.5813	4.1438	0.5963
0.0025	1160.7	839.6	1.2222	22.9016	4.2296	0.6086
0.00125	1158.0	828.5	1.2581	45.4173	4.3408	0.6246
0.000625	1156.1	826.2	1.2672	89.7927	4.4198	0.6360
Ligand L_C						
0.01	1193.3	852.8	1.1523	6.8592	4.5166	0.5940
0.005	1188.7	841.4	1.1883	13.5281	4.6551	0.6123
0.0025	1186.0	835.6	1.2076	26.8665	4.7199	0.6208
0.00125	1184.0	827.8	1.2325	53.3493	4.9020	0.6447
0.000625	1181.0	824.4	1.2459	106.4410	5.0382	0.6626
Ligand L_D						
0.01	1166.1	876.8	1.1155	5.5035	3.8592	0.5875
0.005	1164.3	861.4	1.1575	11.0070	4.0103	0.6105
0.0025	1159.8	848.6	1.1973	22.0140	4.1141	0.6263
0.00125	1156.1	836.4	1.2364	44.0281	4.1712	0.6349
0.000625	1151.6	829.6	1.2617	88.0562	4.2910	0.6532

Fig. 1 to 5: Graphical representation of acoustic parameters in 70% of DMF-water solvent



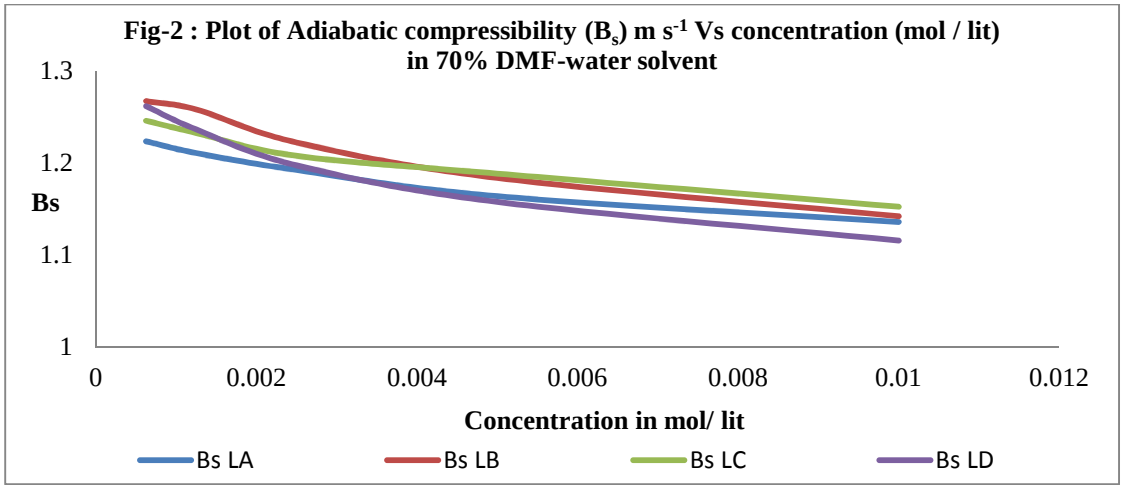


Fig-2 : Plot of Adiabatic compressibility (B_s) m s^{-1} Vs concentration (mol / lit) in 70% DMF-water solvent
1.3
1.2
Bs
1.1
1
0
0.002
0.004
0.006
0.008
0.01
0.012
Concentration in mol/ lit
Bs LA
Bs LB
Bs LC
Bs LD

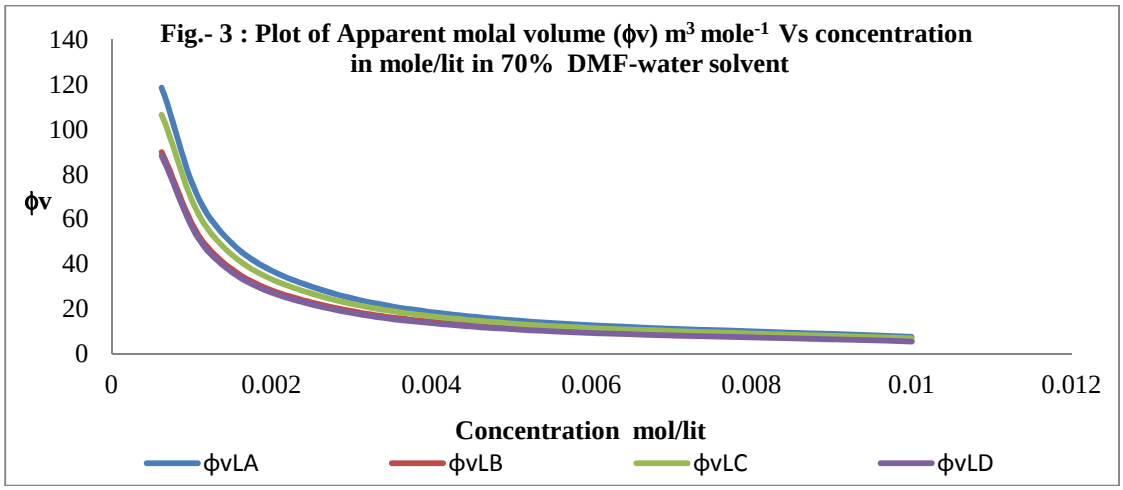


Fig.- 3 : Plot of Apparent molal volume (ϕv) m^3 $mole^{-1}$ Vs concentration in mole/lit in 70% DMF-water solvent
140
120
100
80
ϕv
60
40
20
0
0
0.002
0.004
0.006
0.008
0.01
0.012
Concentration mol/lit
ϕvLA
ϕvLB
ϕvLC
ϕvLD

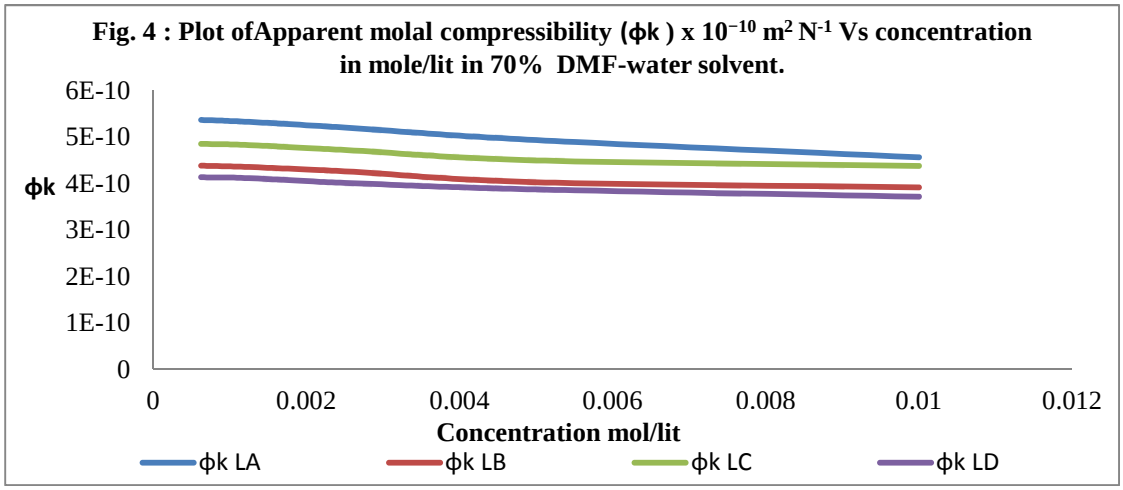


Fig. 4 : Plot ofApparent molal compressibility (ϕk) x 10^{-10} m^2 N^{-1} Vs concentration in mole/lit in 70% DMF-water solvent.
6E-10
5E-10
ϕk 4E-10
3E-10
2E-10
1E-10
0
0
0.002
0.004
0.006
0.008
0.01
0.012
Concentration mol/lit
ϕk LA
ϕk LB
ϕk LC
ϕk LD

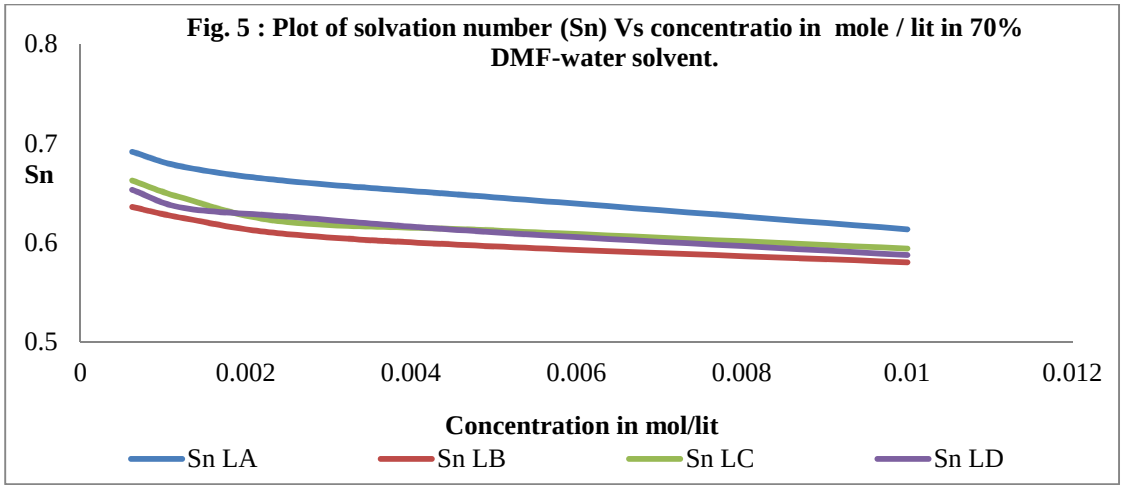


Fig. 5 : Plot of solvation number (Sn) Vs concentratio in mole / lit in 70% DMF-water solvent.

CONCLUSION

The acoustic parameters are helpful to understand the behavior of solute and solvent molecules in solutions. In more concentrated solution the possibility of making hydrogen bond increases which gives packed structure due to this ultrasonic velocity increases. Adiabatic compressibility (β_s) decreases with increase in concentration which shows ion-solvent interaction. The increase in apparent molal volume (ϕ_v) with decrease in concentration indicates the existence of strong ion-solvent interaction. The increase in value of apparent molal compressibility (ϕ_k) with decrease in concentrations shows the weak electrostatic attractive force in the vicinity of ions causing electrostatic salvation of ions. The increase in solvation number (S_n) with decrease in concentration is due to weak solute-solvent interaction in all the systems.

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