Ultrasonic study of substituted 1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid derivatives in 70% DMF-Water

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Abstract

Ultrasonic study of substituted 1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid derivatives in 70% DMF-water at 300K is done. The experimental data is used to calculate intermolecular free length (L_f), specific acoustic impedance (Z), relative association (R_A). These acoustic parameters are used to explain the interaction between the solute and solvent.

Keywords: 1-phenyl-3-aryl-1H-pyrazol-4-carboxylic, acid derivatives, acoustic, solute, solvent

Introduction

The measurements of ultrasonic velocity are useful in study of strength of molecular interaction in the liquid mixture, which provides valuable information regarding internal structure, complex formation, physical nature and molecular association. Ultrasonic study is useful to extensive research specially for investigating various organic liquid-liquid mixture, polymer, metal solvent interaction. The study of certain physical parameter in science and technology, ultrasonic is widely used in recent years for industrial and medicinal application.[1] Ultrasonic study and molecular interaction of drugs in binary mixture are reported.[2-4] Apparant molar volume of NaCl in dioxane, glycol, methanol, ethanol, propane-2-ol, glycerol-water mixture at 10, 20 and 30% within the temperature range 303-313K are studied.[5] The study of acoustical parameters like apparent molar compressibility, relative association, apparent molar volume and solvation number of substituted N, N'bis(salicyliden)-arylmethanediamines in binary mixture of DMF-water is done.[6] Acoustical molecular interaction of azomethine and its Fe(III) metal complex is studied by ultrasonic technique.[7] Ultrasonic technique is used to determined acoustical property of ternary mixture of toluene in cyclohexane and nitrobenzene at 308K.[8] Acoustical parameters of chlorosubstituted pyrazole at different concentration and different percentages in dioxane-water mixture at 305K are reported.[9] Thermodynamic study, adiabatic compressibility, free length and molar volume is reported in ternary liquid systems.[10-14] Acoustic characteristics are reported for sodium salt of N-chloro-p-toluene sulphonamide in aqueous media.[15] The study of acoustical properties of subsitituted thiopyrimidines and substituted oxoimidazoline drugs in 70% (DMF–water) mixture at different concentrations of ligands are studied.[16] Ultrasonic study of 2-hydroxy diethylammonium lactate in different media at 288-323.15K is done.[17] Ultrasonic measurements are done for 2-chlorobenzaldehyde with iodine in hexane ternary solution at 303K in different concentrations.[18] Ultrasonic study of zwitter-ionic nature of amino acids in water is done.[19-20] Ultrasonic velocities of glucose-alcohol-water mixtures are measured at 25^{o}C.[21] Ultrasonic and thermal conductivity study of Cu Onanofluid is done.[22] Ultrasonic measurements of some substituted pyrazolines in acetone-water

are observed with variation of ultrasonic velocity with concentration.[23] Substituted aminopyrimidine in 70% DMF solvent is studied by ultrasonic technique at 300K and different concentration.[24] Ultrasonic study of substituted quinoxaline in ethanol solvent at 305.85 K is reported.[25] Ultrasonic velocity of dilute solutions of caffeine, l-methyl-4-(methylamino) pyrazol[3,4-d]pyrimidine, adenosine, and deoxyadenosine at a different temperatures are determined.[26] Ultrasonic velocity, density and viscosity for aqueous solution of NaCl at different concentrations and at different frequencies at constant temperature (293K) are measured.[27] Measurement of ultrasonic velocity and density of N-methylformamide, N,N-dimethylformamide and N,N-dimethylacetamide in aqueous solutions at 25 and 35^0C are reported.[28] Ultrasonic study of substituted 2-oxo-2*H*-chromene-3 carbohydrazide derivatives in 70% DMF-Water is reported.[29] Density and ultrasonic velocity of N,N-dimethylformamide, cyclohexane and benzene at temperature 318 K are measured.[30]

The present work is used to determine intermolecular free length (L_f), specific acoustic impedance(Z), relative association (R_A) and of following substituted 1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid derivatives in 70% (DMF+water) mixture at different concentrations of ligands at 300K.

i) Ligand A (LA)= 1- phenyl-3-(4'- methyl) phenyl-1H- pyrazol-4-carboxylic acid
ii) Ligand B (LB)= 1- phenyl-3-(4'- bromo) phenyl-1H- pyrazol-4-carboxylic acid
iii) Ligand C (LC)= 1- phenyl-3-(4'- ethyl) phenyl-1H- pyrazol-4-carboxylic acid
iv) Ligand D (LD)= 1,3-diphenyl-1H- pyrazol-4-carboxylic acid

Materials and Methods

All the chemicals used are of analytical 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) with 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 27^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.[31]

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[32-33] of solvent and solution can be calculated by using equations:

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

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

The acoustic impedance (Z)[34] is calculated using equation:

Acoustic impedance (Z) = Us x ds (5)

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]

$$\text{Apparent molal volume } (\phi_v) = \frac{M}{d_s} + \frac{(d_0 - d_s) \times 10^3}{(m d_s d_0)} \quad (6)$$

$$\text{Apparent molal compressibility } (\phi_k) = \frac{1000(\beta_s d_0 = \beta_0 d_s)}{m d_s d_0} + \frac{\beta_s M}{d_s} \quad (7)$$

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.

According to the studies intermolecular free length (L_f)[36] is given by:

Intermolecular free length (L_f) = $K\sqrt{\beta s}$ (8)

The constant K is called the Jacobson's constant.

The value of Jacobson's constant can be calculated by using relation

$K = (93.875 + 0.375 \times T) \times 10^{-8}$ (9)

Where, T is the temperature at which experiment is carried out.

The relative association (R_A)[37-38] is given by the equation:

$$\text{Relative association } (R_A) = \left(\frac{d_s}{d_0}\right) \times \left(\frac{U_0}{U_s}\right)^{1/3} \quad (10)$$

The solvation number (S_n)[39] is given by the equation.

Solvation number (S_n) = $\phi_k / \beta_0 \times (M / d_0)$ (11)

In present works the measurement of ultrasonic velocity and density at a different concentration of substituted 1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid derivatives in 70% DMF+water solvent is carried out at 300K. The data obtained is used to determine different acoustical parameters such as intermolecular free length (L_f), specific acoustic impedance (Z) and relative association (R_A). The formula No. 05, 08 and 10 are used for calculations.

From table no. 1 it is observed that ultrasonic velocity decreases with decreases in concentration in this system. Ultrasonic velocity increases on increasing the concentration of solute may be attributed to cohesion brought about by the association among the molecule and greater solute - solvent interaction. In more concentrated solution the possibility of making hydrogen bond increases which gives packed structure due to this ultrasonic velocity increases. Fig. no. 01 shows the variation of ultrasonic velocity with concentration.

Table no. 1 suggests that intermolecular free length is more in more dilute solution. Fig. no. 2 shows the variation of intermolecular free length (L_f) with concentration. In many cases, the value of L_f corresponds to the molecular shape, that is the L_f in the molecules having the spherical and/or symmetrical shape is short and the short L_f leads to a high speed of sound. Decrease in intermolecular free length leads to positive deviation in sound velocity and negative deviation in compressibility.

Table no. 1 suggests that as the concentration increases the specific acoustic impedance increases. Fig. no. 3 shows the variation of specific acoustic impedance (Z) with concentration. Increase in specific

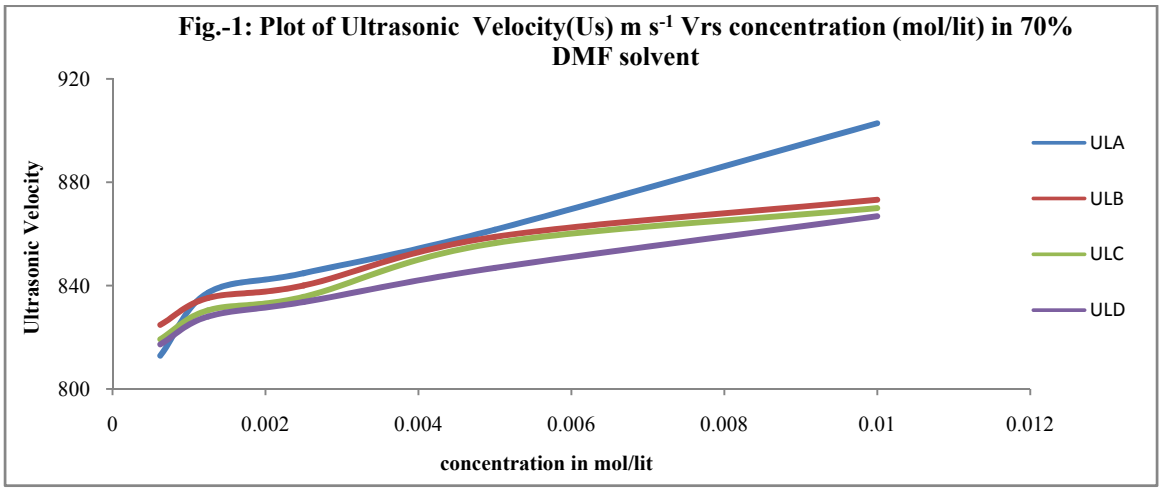
acoustic impedance with increase in concentration suggests associative molecular interactions in all the systems.

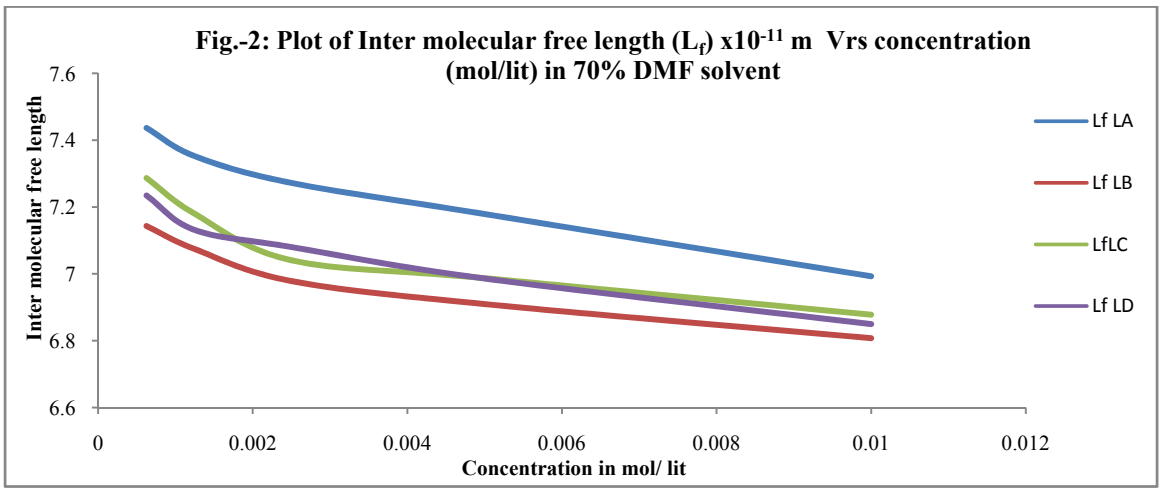
Table no. 1 shows that relative association (R_A) increases as the concentrations decreases. Fig. no. 4 shows the variation of relative association with concentrations. Relative association (R_A) is the property use to understand the solute and solvent interaction. It is found that there is weak solute-solvent interaction.

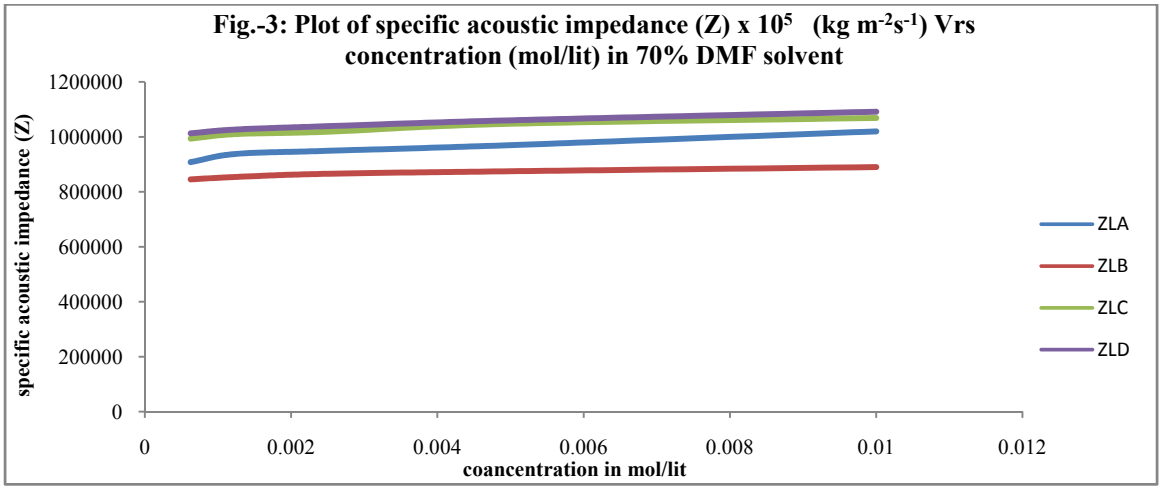
Table 1 : Density(d), ultrasonic Velocity (U_s), intermolecular free length (L_f), specific acoustic impedance (Z) and relative association (R_A) in 70% (DMF+Water) solvent at 300K

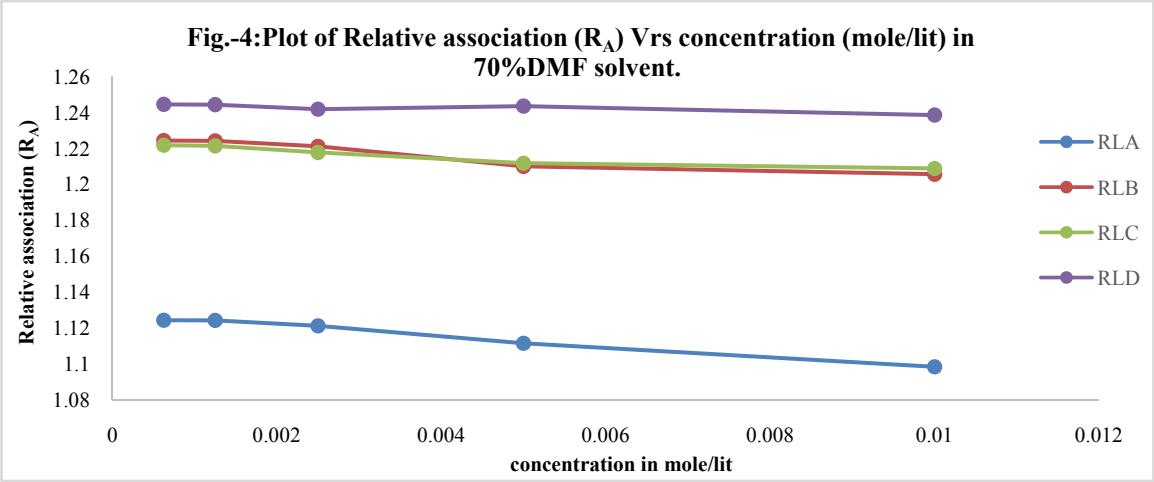
Conc. (m) (mol lit^{-1})	Density (d) (kg m^{-3})	Ultrasonic Velocity (U_s) (m s^{-1})	Intermolecular free length (L_f) x 10^{-11} (m)	Specific acoustic impedance (Z) x 10^5 (kg m^{-2}s^{-1})	Relative association (R_A)
Ligand LA					
0.01	1127.8	898.0	6.8432	10.127	1.1777
0.005	1123.6	864.4	7.1225	9.715	1.1348
0.0025	1121.0	836.0	7.3730	9.371	1.1080
0.00125	1118.8	831.2	7.4229	9.299	1.0986
0.000625	1116.8	826.0	7.4767	9.224	1.0883
Ligand LB					
0.01	1226.6	874.4	6.7390	10.720	1.1950
0.005	1222.3	860.4	6.8600	10.516	1.1566
0.0025	1219.6	836.8	7.0619	10.205	1.1610
0.00125	1216.5	828.8	7.1390	10.082	1.1459
0.000625	1226.6	874.4	7.7390	10.720	1.1360
Ligand LC					
0.01	1227.5	862.8	6.8270	10.597	1.1659
0.005	1223.5	852.4	6.9216	10.425	1.1521
0.0025	1219.9	834.0	7.0848	10.173	1.1396
0.00125	1216.8	824.0	7.1790	10.026	1.1227
0.000625	1212.9	821.2	7.2159	9.960	1.1210
Ligand LD					
0.01	1255.2	861.6	6.7607	10.8148	1.1539
0.005	1251.0	846.0	6.8969	10.583	1.1402
0.0025	1247.6	832.4	7.0192	10.385	1.1327
0.00125	1245.5	822.0	7.1139	10.238	1.1303
0.000625	1243.9	820.4	7.1324	10.204	1.1156

Fig. 1 to 4: Graphical representation of acoustic parameters in 70% of DMF-water solvent









Conclusion

The acoustic parameters are helpful to understand the behavior of solute and solvent molecules in solutions. Specific acoustic impedance (Z) increases with increase in concentration indicates that there is associative molecular interaction. Relative association (R_A) and Intermolecular free length (L_f) is the property useful to understand the solute-solvent interaction.

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