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Studies in acoustical properties of chloro subsitituted pyrazoles in different concentration and different percentages in dioxane–water mixture

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ABSTRACT

The acoustical properties of chlorosubstituted pyrazoles have been investigated from the ultrasonic velocity and density measurements at different concentration and different percentages in dioxane-water mixture at 305^0 k. The adiabatic compressibility (β_s), acoustic impedence (Z), inter molecular free length (L_f), apparent molal volume (ϕ_v) and relative association (R_A) values have been calculated from the experimental data of velocity and density measurement at concentration range 0.01-0.000625 mol/lit and 70%, 75%, 80% dioxane-water mixture. These above parameters are used to discuss the structural and molecular interactions.

Keywords: Acoustical parameters; Ultrasonic velocity; Density; Chloro substituted pyrazoles; Dioxane-water mixture.

INTRODUCTION

Ultrasonic wave's means sound waves hearing above range of normal ear. The study of inter molecular interaction plays an important role in the development of molecular Sciences. The nature and relative strength of the molecular interaction between the components of the liquid mixtures have been studied by the ultrasonic method [1, 2]. A large number of studies have been made on the molecular interaction in liquid mixtures by various physical methods like Ultra-violent [3], Infrared [4, 5]. Nuclear Magnetic resonance, Dielectric constant [6], Raman effect [7] and ultrasonic method [8, 9]. For interpreting solute-solvent, ion-solvent interaction in aqueous and non – aqueous medium was helpful from Ultrasonic velocity measurements in recent year [10-13]. Ultrasonic waves used to detect a wide variety of anomalous condition such as pregnancy, tumors and a study various phenomena such as heart valve action. This Ultrasonic wave is more sensitive than X-rays. Due to this ultrasonic technique used in the treatment of certain cancer as well as arthritis and related diseases [14]. Recently, the acoustical properties of amino acids in aqueous magnesium acetate at constant temperature were studied from the measurement of ultrasonic velocity and density [15]. The studied of the determination of densities, viscosities, refractive indices of organic liquid mixture are reported by many workers

[16-19]. The studied the acoustical properties and viscosity coefficient of substituted heterocyclic drugs under suitable condition [20]. Substituted pyrazoles and their derivatives have received much attention towards their application in agro chemicals industries [21] and medicinal values [22]. The chlorosubstituted pyrazoles and pyrazolines act as an antimicrobial drugs [23] and in view of applications in various field. The work follow systematic studies of chlorosubstituted pyrazoles in different concentration and different percentage in dioxane-water mixture and measure the ultrasonic velocities and densities, from that values, evaluated the acoustic properties.

MATERIALS AND METHODS

All chemicals used were of analytical grade was purified by Vogel's standard method [24]. The distilled dioxane was used for preparation of different concentration and different percentages of chorosubstituted pyrazoles solution. Acetone was used for washing purpose. The acoustical properties require the measurement of ultrasonic velocity and densities. The densities of pure solvent and their solution were measured by using a bicapillary Pyknometer (Borosil) (± 0.2%) having a bulb volume of about 10 cm^3 and capillary having an internal diameter of 1 mm. The ultrasonic velocities were measured by using single crystal interferometer (Mittal Enterprises, Model MX-3) with accuracy of ± 0.03 % and frequency 2MHz. A special thermostatic arrangement were done for Elite thermostatic water bath were used in which conditions stirring of water was carried out with the help of electric stirrer. In the present work, different properties such as adiabatic compressibility (β_s), apparent molal volume (ϕ_v), inter molecular free length (L_f), apparent molal compressibility (ϕ_k), acoustic impedance (Z), relative association (R_A) have been evaluated from following equations.

The adiabatic compressibility (β_s) was calculated from Newton-Laplace.
Equation:

$$\beta_s = 1/U_s^2 \times d_s \;\;\ldots\ldots\ldots \text{[for solution]} \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\beta_o = 1/U_o^2 \times d_o \;\;\ldots\ldots\ldots \text{[for solvent]} \ldots\ldots\ldots\ldots\ldots\ldots (1a)$$

Where, d_o, d_s and U_o, U_s are the densities of pure solvent, solution and ultrasonic velocities of pure solvent and solutions, respectively

The apparent molal compressibility (ϕ_k) has been calculated by using the relation.

$$\phi_k = \frac{1000\,(\beta s \times do - \beta o \times ds)}{m \times ds \times do} + \frac{\beta s \times M}{ds} \quad \ldots\ldots.(2)$$

The apparent molal volume (ϕ_v) has been calculated by using the relation.

$$\phi_v = \frac{M}{d_s} + \frac{(d_o - d_s) \times 10^3}{m \times d_s \times d_o} \quad \ldots\ldots\ldots\ldots\ldots(3)$$

Where, 'M' is the molecular weight of solute and 'm' is the molality of the solute.

The inter molecular free length (L_f) is calculated by using the standard expression-

$$L_f = K \times \sqrt{\beta_s} \;\;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where 'K' is a temperature dependent constant known as Jacobson constant [25].

The relative association (R_A) was calculated by the following equation.

$$R_A = \left[\frac{d_s}{d_o}\right]\left[\frac{U_o}{U_s}\right]^{1/3} \quad \text{.....................(5)}$$

The acoustic impedance (Z) is obtained by the following relation

$$Z = Us \times ds \text{ ---------------- (6)}$$

RESULT AND DISCUSSION

The experimental values of density and ultrasonic velocity at different concentration of ligand (L_1 & L_2) and different percentage in dioxane -water mixtures at 305^0 K are given in the tables 1, 2. From these experimental

Table 1. Values of density and ultrasonic velocity at different concentration of ligand L_1 and L_2 at 305^0 K

Concentration (mole/lit.)	√c	Density (g/cm^3)		Ultrasonic Velocity (m/sec)	
		L_1	L_2	L_1	L_2
0.01	0.100	1.02757	1.02812	1447.5	1467.0
0.005	0.070	1.02315	1.02270	1481.7	1464.0
0.0025	0.050	1.02599	0.99322	1491.5	1449.0
0.00125	0.035	1.02696	0.99046	1492.5	1466.0
0.000625	0.025	1.02926	0.93969	1499.1	1480.0

Table 2 : Values of density and Ultrasonic Velocity at different percentages in dioxone – water mixture in 305^0 K

% of Dioxane	Density (g/cm^3)		Ultrasonic Velocity (m/sec)	
	L_1	L_2	L_1	L_2
70%	1.02757	1.02812	1452.8	1467.0
75%	1.02316	1.03989	1447.5	1440.0
80%	1.0224	1.02129	1432.4	1417.0

Where,
L_1 = 3 – (2 – Hydroxy – 3,5 dichlorophenyl) -4 – anisoyl – 5 (4 – methoxy phenyl) – 1 – phenyl pyrazole.
L_2 = 4 – (2 - chlorophenyl) – 3-(4 – Chlorophenyl)-5 – (2 – Hydroxy phenyl) pyrazole.
values have been used to determined the acoustical properties of chlorosubstituted pyrazoles at different concentration and different percentage are given in tables 3, 4, 5 and 6 respectively.

Table 3. Acoustic properties of Ligand (L_1) of different concentrations in dioxane-water mixture at 305^0 K

Different conc. (mol.lit^{-1})	β_s x 10^{-7} (bar^{-1})	ϕ_v x 10^2 (cm^3.mol^{-1})	ϕ_k x 10^{-4} (cm^3.mol^{-1}. bar^{-1})	Lf x 1((A^0)	R_A	Z X 10^2 cm.sec^{-1}.g. cm^{-3}
0.01	4.6446	5.0321	2.3395	4.3345	1.0177	1487.41
0.005	4.4518	5.0545	2.2503	4.2435	1.0055	1516.01
0.0025	4.3814	5.0405	2.2085	4.2098	1.0062	1530.26
0.00125	4.3714	5.0357	2.2013	4.2051	1.0068	1532.73
0.000625	4.3233	5.0245	2.1723	4.1818	1.0076	1542.96

Table 4 : Acoustic Properties of Ligand (L_2) of different concentration in dioxane-water mixture at 305^0 K

Different conc. ($mol.lit^{-1}$)	$\beta_s \times 10^{-7}$ (bar^{-1})	$\phi_v \times 10^2$ ($cm^3.mol^{-1}$)	$\phi_k \times 10^{-4}$ ($cm^3.mol^{-1}.bar^{-1}$)	Lf x 1((A^0)	R_A	Z X 10^2 $cm.sec^{-1}.g.cm^{-3}$
0.01	4.5195	3.9774	1.7986	4.2756	1.0137	1508.25
0.005	4.5622	3.9993	1.8245	4.2957	1.0092	1497.24
0.0025	4.7954	4.1181	1.9748	4.4042	0.9137	1439.7
0.00125	4.6978	4.1296	1.9403	4.3592	0.9768	1452.02
0.000625	4.8584	4.3525	2.1146	4.4331	0.9238	1390.75

Table No. 5 : Acoustic properties of ligand (L_1) of different percentages in dioxane – water mixture at 305^0 K

% of Dioxane	$\beta_s \times 10^{-7}$ (bar^{-1})	$\phi_v \times 10^2$ ($cm^3.mol^{-1}$)	$\phi_k \times 10^{-4}$ ($cm^3.mol^{-1}.bar^{-1}$)	Lf x 1((A^0)	R_A	Z X 10^2 $cm.sec^{-1}.g.cm^{-3}$
70%	4.618	5.0321	2.3222	4.3186	1.0165	1492.85
75%	4.6646	5.0534	2.3576	4.3437	1.0154	1481.03
80%	4.7671	5.0585	2.4126	4.3912	1.0023	1464.48

Table 6 : Acoustic properties of ligand (L_2)of different concentrations in dioxane – water mixture at 305^0 K

% of Dioxane	$\beta_s \times 10^{-7}$ (bar^{-1})	$\phi_v \times 10^2$ ($cm^3.mol^{-1}$)	$\phi_k \times 10^{-4}$ ($cm^3.mol^{-1}.bar^{-1}$)	Lf x 1((A^0)	R_A	Z X 10^2 $cm.sec^{-1}.g.cm^{-3}$
70%	4.5195	3.9774	1.7986	4.2756	1.0137	1508.25
75%	4.6375	3.9304	1.8219	4.3312	1.0337	1497.45
80%	4.8765	4.0051	1.9554	4.4414	1.0047	1447.16

The various acoustical properties like adiabatic compressibility (β_s), apparent molal volumes (ϕ_V), apparent molal compressibility (ϕ_K), inter molecular free length (Lf), relative association (R_A) and specific acoustic impedance (Z) are calculated using equation (1)–(6) and which are represented in tables 3 to 6.

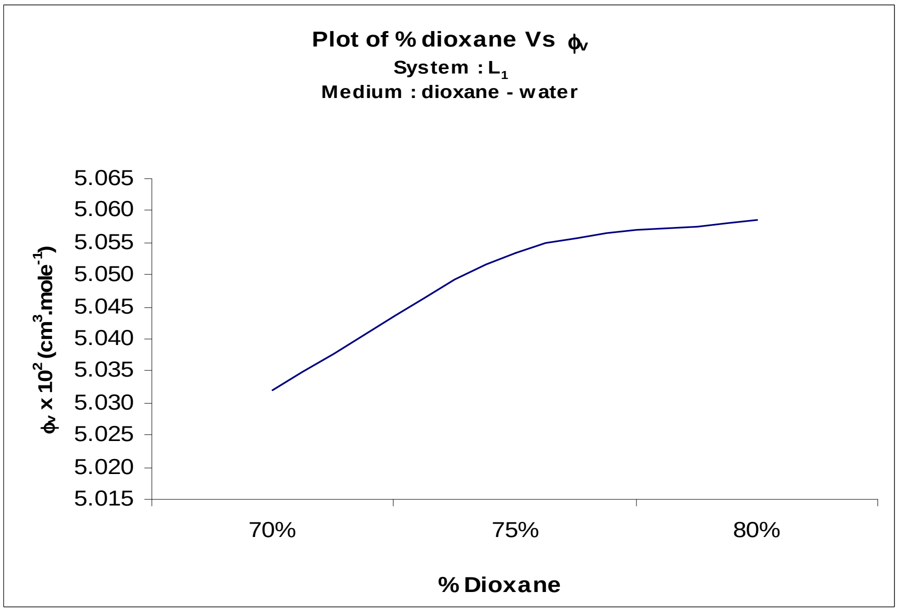

Fig.1. Effect of percentage of Dioxane-water mixture on L_1

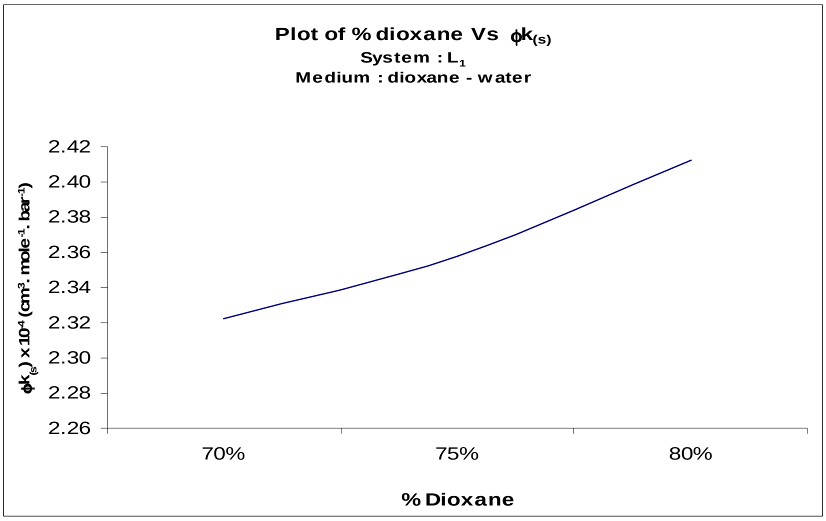

Fig. 2 Effect of percentage of Dioxane-water mixture on L_1

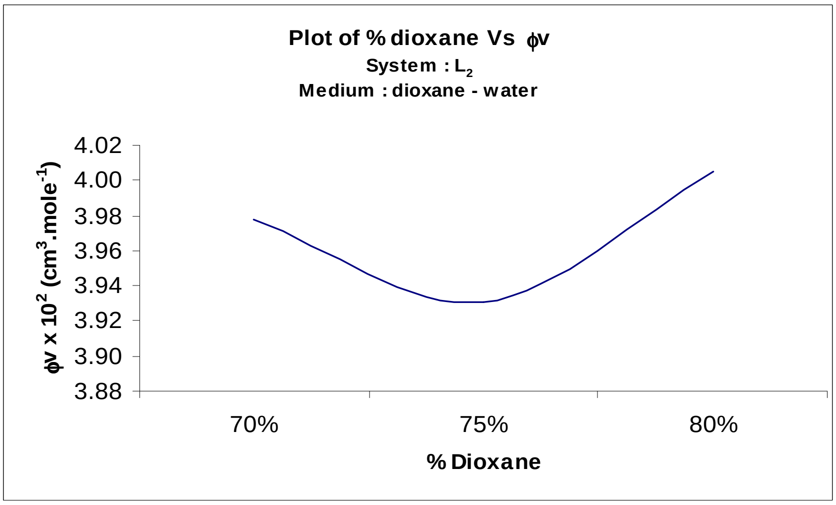

Fig. 3 Effect of percentage of Dioxane-water mixture on L_2

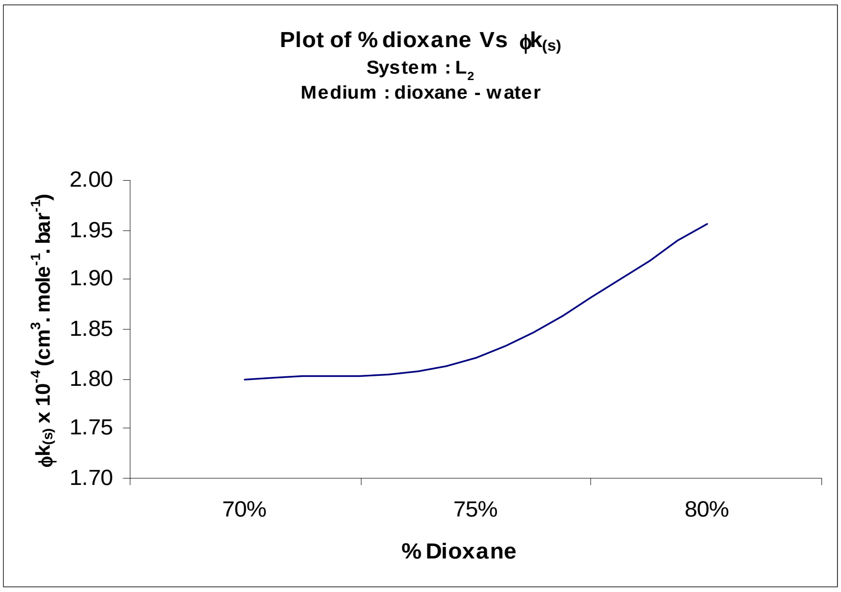

Fig. 4 Effect of percentage of Dioxane-water mixture on L_2

The values of ϕ_k and ϕ_V have been used to discuss the interaction of unlike molecule of solvents in presence of solute. The graph of ϕ_V and ϕ_k against percentage of dioxane are given in fig. 1 to 4 and from the graph, the values of apparent molal volumes (ϕ_V) and apparent molal compressibility (ϕ_k) are increased with increase in % of dioxane for ligand L_1 and L_2 irregularly. The table-5 and 6 showed adiabatic compressibility (β_s) increased with increase in percentages of dioxane–water mixtures. The intermolecular free length (L_f) is found to be similar behavior, increase in free length results decrease ultrasonic velocity on the basis of sound propagation in the liquid [26, 27]. This is in good concordance with Naik and Co-workers [28]. These results showed that there is weak solute-solvent interaction.

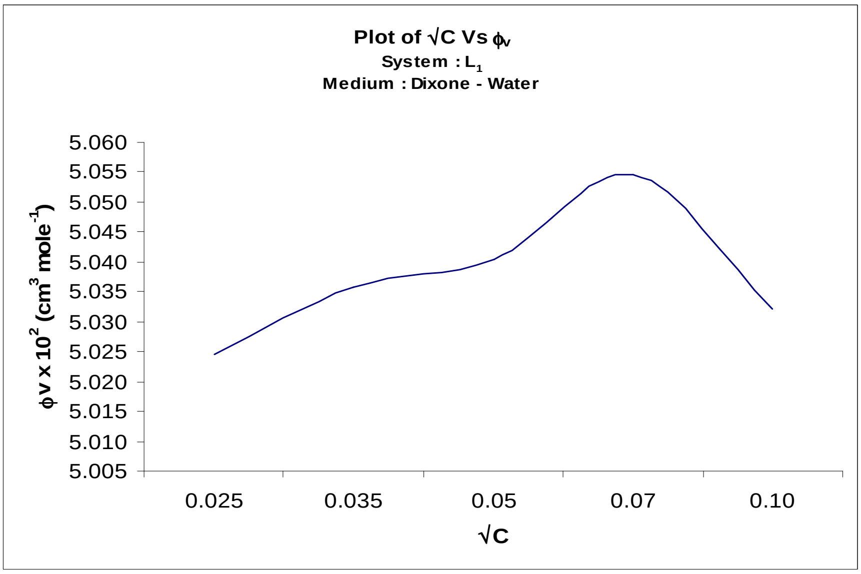

Fig. 5 Effect of concentration of L_1 in Dioxane-water mixture on apparent molal volume

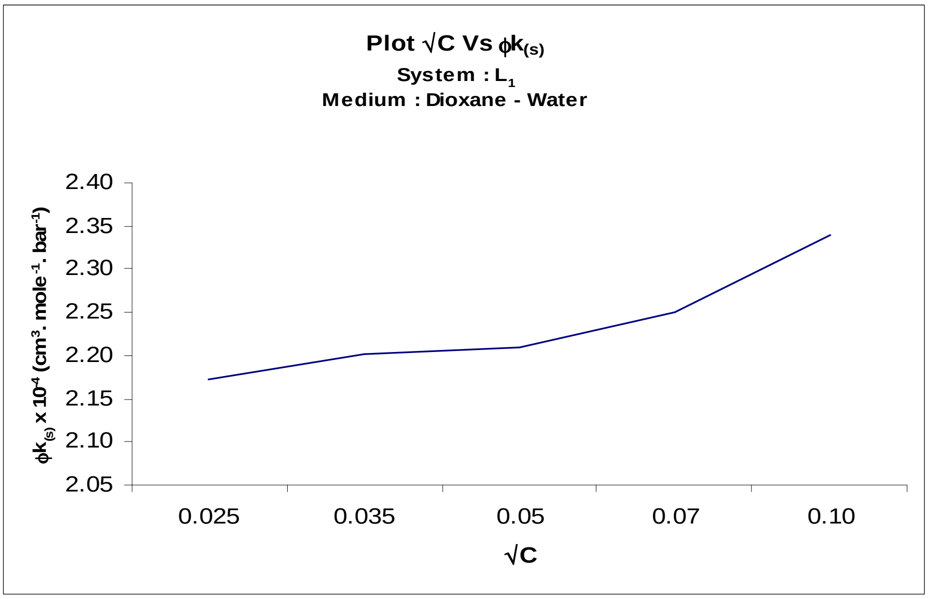

Fig. 6 Effect of concentration of L_1 in Dioxane-water mixture on apparent molal compressibility

It could be seen from fig. 5 and 6 that, the apparent molal volume and apparent molal compressibility are increased with increase in concentrations of ligand L_1 and decreased with increase in concentrations for ligand L_2. This may be due to the presence of chlorine group nearer to the hydroxyl group in ligand–L_1 but in ligand-L_2 away from the hydroxyl group. The table (3) and (4), the values of adiabatic compressibility showed that, it decreased with decrease in concentrations of ligand L_1 & vice-versa for ligand L_2. The intermolecular free length also observed similar behavior. This indicates there is weak solute-solvent interaction. The relative association and acoustic impedance are decreased linearly with increase in percentages of dioxane–water mixtures and decreased in concentration of ligands-L_1 and L_2. This results showed solute-solvent interaction [29] may occur in the system.

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