Scientific Reviews & Chemical Communications

Sci. Revs. Chem. Commun.: 4(3), 2014, 91-100
ISSN 2277-2669

ULTRASONIC INTERFEROMETRIC INVESTIGATIONS OF 3-(CHLOROARYL)-5-ARYL-1-SUBSTITUTED PYRAZOLINES IN DIOXANE MEDIUM

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(*Received : 19.05.2014; Revised : 27.05.2014; Accepted : 28.05.2014*)

ABSTRACT

Ultrasonic velocity and density measurements of ligand, 3-(Chloroaryl)-5-aryl-1-substituted Pyrazolines were carried out at different percentage of dioxane solvents for investigating solute-solvent, solute-solute interaction at different temperature 293 K 297 K, and 300 K. The data obtained during the study is used for determing most significant acoustic parameters like Velocity (v), Density (d), Adiabatic compressibility (β) Apparent molar compressibility (ϕ_k), Apparent molar volume (ϕ_v). The parameters explore solute–solute and solute-solvent interactions in different solvents. In this investigation, the comparative study of effect of solvents and effect of substituents in the solute are studied on molecular interaction of the matter.

Key words: Substituted pyrazolines, Acoustic parameters, Interferometry, Solute-solvent interaction.

INTRODUCTION

Ultrasonic studies on molecular interaction and physico-chemical behaviour of some divalent transition metal sulphates in aqueous propylene glycol at 303.15 K have been studied by Palani et al.[1] Apparant molar volume of NaCl have been studied in Ethanol, Methanol, Propane-2-ol, Dioxane, Glycol, Glycerol water mixture at 10, 20 and 30% (W/W) within the temperature range 30-40^{o}C and ion solvent interaction has been inferred[2]. Speeds of sound & isentropic compressibillities[3] for binary mixtures of 1,2-ethane diol with 1-butanol, 1-hexanol, or 1-octanol in the temperature range from 293.15 to 313.15 K. Ultrasound assisted[4] the chemoselective 1,1-diacetate protection and deprotection of aldehydes catalyzed by poly (4-vinyl pyridinum) hydrogen sulfate salt as a eco-benign efficient and reusable solid acid catalyst. Acoustical studies on ternary mixture of toluene in cyclohexane and nitrobenzene at 308 K using ultrasonic technique have been studied by Mistry et al.[5]

The use of ultrasound is one of the well recognized approaches for the study of molecular interactions in fluids. The ultrasonic velocity plays an important role in the investigation of intermolecular interactions. Weak molecular interactions can also be studied by ultrasonic technique. The structural arrangement are influenced by the shape of the molecules as well as mutual interactions. The ultrasonic velocity and other acoustic parameters can be measured with great accuracy and consequently provides a powerful way to determine intermolecular interactions.

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Hence, in this present investigation attempt is made to understand behaviour of substituted –

(i) 3-(2-Hydroxy-5-chlorophenyl)-5-phenyl-1-thiocarboxamido pyrazoline (L_1)

(ii) 3-(2-Hydroxy-5-chlorophenyl)-5-(3-chlorophenyl)-1-thiocarboxamido pyrazoline (L_2)

(iii) 3-(2-Hydroxy-3-bromo-5-chlorophenyl)-5-phenyl-1-thiocarboxamido pyrazoline (L_3)

(iv) 3-(2-Hydroxy-3-bromo-5-chlorophenyl)-5-(3-chlorophenyl)-1-thiocarboxa-mido pyrazoline (L_4)

(v) 3-(2-Hydroxy-3-nitro-5-chlorophenyl)-5-phenyl-1-thiocarboxamido pyrazoline (L_5)

(vi) 3-(2-Hydroxy-3-nitro-5-chlorophenyl)-5-(3-chlorophenyl)-1-thiocarboxa-mido pyrazoline (L_6)

Compounds at different percentage of dioxane solvent separately, The ultrasonic velocity and densites of 0.01 M solutions of different percentage of dioxane solvent of L1, L2, L3, L4, L5 and L6 were determined from these β_s, ϕ_k, ϕ_v, were calculated.

EXPERIMENTAL

All the chemicals were of A. R. grade. Double-distilled water was used during the study. The six ligands were synthesized in our laboratory by reported methods.[6] The solvent 1,4-dioxane were purified by standard procedure.[7] Densities were measured with the help of bicapillary pyknometer, 0.01 M solution of ligand at different percentage of dioxane solvent were prepaired seperatly. Weighing was made on Mechaniki Zaktady Precynyneij Gdansk balance made in Poland (± 0.001 g). A special thermostatic arrangement was done for density and ultrasonic velocity measurements. Elite thermostatic water bath was used, in which continuous stirring of water was carried out with the help of electric stirrer and temperature variation was maintained within ± 0.1°C. Single crystal interferometer (Mittal Enterprises, Model MX-3) with accuracy of ± 0.035% and frequency of 1 MHz was used in the present work. The densities and ultrasonic velocity of ligands L1, L2, L3, L4, L5 and L6 in dioxane solvent at different temperature i.e. 293 K, 297 K, 300 K.

The Adiabatic compressibility of solvent (β_0) and (β_s) are given by –

$\beta_0 = 1/(v_0^2\, d_0)$ and $\beta_s = 1/(v_s^2\, ds)$

v_0, d_0, v_s and d_s are ultrasonic velocity and densities of solvent and solutions respectively.

Apparent molar compressibility (ϕ_k) was obtained from,

$(\phi_k) = 1000\ (\beta_s\, d_o - \beta_0\, d_s)/\ C\ d_s\, d_o + (\beta_s\, M/d_s)$

Apparent molar volume (ϕ_v) has been calculated from the relation.

$(\phi_v) = 1000\ (d_o - d_s)/Cd_s\, d_o + M/d_s$

M = Molecular weight of ligand and C = Molarity of the solution

All these acoustic parameters were computed for all the six ligands at different percentage of 1,4-dioxane.

RESULTS AND DISCUSSION

A study of β, ϕ_k, and ϕ_v directly relate the structural interaction of solvent with solute and provides the information regarding complex formation, stability, internal structure, molecular association and internal pressure. The values of acoustic parameters are given in Table 1 to 18.

Table 1: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand - L_1 Temp. = 293 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V ($m. sec^{-1}$)	ds x 10^3 ($Kg.m^{-3}$)	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} (m^3 mol^{-1} pa^{-1})	ϕ_v (m^3mol^{-1})
70	1597.00	0.887	4.4205	-11.9532	116.1345
75	1599.06	0.889	4.3992	-12.3061	-138.3323
80	1521.31	0.893	4.8385	-7.5929	-643.8464
85	1534.86	0.893	4.7535	-8.5479	-643.8464
90	1454.77	0.890	5.3091	-2.1046	-265.1368

Table 2: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_2 Temp. = 293 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V ($m. sec^{-1}$)	ds x 10^3 ($Kg.m^{-3}$)	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} (m^3 mol^{-1} pa^{-1})	ϕ_v (m^3mol^{-1})
70	1601.032	0.889	4.3883	-12.4123	-100.0871
75	1520.72	0.893	4.8423	-7.5318	-605.7725
80	1511.640	0.892	4.9061	-6.7529	-479.7763
85	1447.816	0.892	5.3482	-1.7786	-479.7763
90	1453.124	0.891	5.3152	-2.0828	-353.4973

Table 3: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_3 Temp. = 293 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V ($m. sec^{-1}$)	ds x 10^3 ($Kg.m^{-3}$)	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} (m^3 mol^{-1} pa^{-1})	ϕ_v (m^3mol^{-1})
70	1573.984	0.890	4.5353	-10.7955	-194.3503
75	1519.456	0.893	4.8503	-0.5510	-573.2977
80	1496.136	0.892	5.0083	-5.5867	-447.2651
85	1518.800	0.892	4.8600	-7.2561	-447.2651
90	1437.600	0.893	5.4184	-1.0394	-573.2977

Table 4: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_4 Temp. = 293 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V ($m. sec^{-1}$)	ds x 10^3 ($Kg.m^{-3}$)	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} (m^3 mol^{-1} pa^{-1})	ϕ_v (m^3mol^{-1})
70	1560.512	0.891	4.6088	-9.9989	-264.8329
75	1521.760	0.893	4.8357	-7.5631	-517.3066
80	1497.432	0.894	4.9885	-5.9073	-643.1199
85	1516.880	0.892	4.8723	-7.0900	-391.2113
90	1496.160	0.891	5.0136	-5.4333	-264.8329

Table 5: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_5 Temp. = 293 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V (m. sec^{-1})	ds x 10^3 (Kg.m^{-3})	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} (m^3 mol^{-1} pa^{-1})	ϕ_v (m^{3}mol^{-1})
70	1586.768	0.890	4.4626	-11.6246	-214.5750
75	1515.792	0.893	4.8738	-7.1717	-593.4544
80	1519.960	0.892	4.8526	-7.3489	-467.4445
85	1577.040	0.891	4.5127	-11.1167	-341.1516
90	1455.528	0.890	5.3036	-2.1398	-214.5750

Table 6: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_6 Temp. = 293 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V (m. sec^{-1})	ds x 10^3 (Kg.m^{-3})	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} (m^3 mol^{-1} pa^{-1})	ϕ_v (m^{3}mol^{-1})
70	1587.328	0.892	4.4494	-11.8690	-429.3279
75	1572.288	0.893	4.5299	-11.0199	-555.3805
80	1561.904	0.894	4.5852	-10.4558	-681.1512
85	1578.312	0.894	4.4903	-11.5217	-681.1512
90	1508.00	0.890	4.9409	-6.2114	-176.3728

Table 7: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand - L_1 Temp. = 297 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V (m. sec^{-1})	ds x 10^3 (Kg.m^{-3})	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} (m^3 mol^{-1} pa^{-1})	ϕ_v (m^{3}mol^{-1})
70	1678.600	0.887	4.0011	-24.3273	-268.2000
75	1520.648	0.886	4.8810	-14.6996	-140.5358
80	1521.715	0.891	4.8468	-15.0076	-775.9912
85	1520.352	0.890	4.8610	-14.7868	-649.4713
90	1518.720	0.889	4.8769	-14.5451	-522.6668

Table 8: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_2 Temp. = 297 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V (m. sec^{-1})	ds x 10^3 (Kg.m^{-3})	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} (m^3 mol^{-1} pa^{-1})	ϕ_v (m^{3}mol^{-1})
70	1647.016	0.887	4.1560	-22.5593	-229.8686
75	1520.648	0.890	4.8591	-14.7891	-611.2691
80	1498.232	0.888	5.0168	-12.8833	-357.2884
85	1522.080	0.886	4.8718	-14.3978	-102.1611
90	1510.792	0.885	4.9505	-13.4430	25.8350

Table 9: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_3 Temp. = 297 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V ($m. sec^{-1}$)	ds x 10^3 ($Kg.m^{-3}$)	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} ($m^3 mol^{-1} pa^{-1}$)	ϕ_v (m^3mol^{-1})
70	1566.768	0.891	4.5721	-18.0685	-705.2841
75	1519.640	0.889	4.8710	-14.5774	-451.8007
80	1483.736	0.888	5.1153	-11.7534	-324.6308
85	1525.776	0.887	4.8428	-14.7724	-197.1741
90	1438.880	0.887	5.4454	-7.9520	-197.1741

Table 10: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_4 Temp. = 297 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V ($m. sec^{-1}$)	ds x 10^3 ($Kg.m^{-3}$)	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} ($m^3 mol^{-1} pa^{-1}$)	ϕ_v (m^3mol^{-1})
70	1585.272	0.887	4.5031	-18.5918	-140.8043
75	1520.256	0.889	4.8670	-14.5950	-395.5577
80	1520.784	0.889	4.8637	-14.6329	-395.5577
85	1573.832	0.888	4.5464	-18.1594	-268.3244
90	1520.632	0.886	4.8811	-14.2490	-12.9963

Table 11: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_5 Temp. = 297 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V ($m. sec^{-1}$)	ds x 10^3 ($Kg.m^{-3}$)	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} ($m^3 mol^{-1} pa^{-1}$)	ϕ_v (m^3mol^{-1})
70	1680.048	0.890	3.9808	-24.6885	-598.9095
75	1494.064	0.889	5.0392	-12.6880	-472.0481
80	1437.896	0.888	5.4467	-8.0178	-344.9010
85	1573.808	0.888	4.5466	-18.1920	-344.9010
90	1437.120	0.886	5.4649	-7.6726	-89.7458

Table 12: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_6 Temp. = 297 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V ($m. sec^{-1}$)	ds x 10^3 ($Kg.m^{-3}$)	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} ($m^3 mol^{-1} pa^{-1}$)	ϕ_v (m^3mol^{-1})
70	1600.712	0.888	4.3950	-19.8887	-306.6127
75	1521.128	0.888	4.8669	-14.5529	-306.6127
80	1501.112	0.888	4.9976	-13.0750	-306.6127
85	1519.312	0.888	4.8786	-14.4206	-306.6127
90	1442.480	0.887	5.4182	-8.2501	-179.1358

Table 13: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand - L_1 Temp. = 300 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V ($m. sec^{-1}$)	ds x 10^3 ($Kg.m^{-3}$)	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} ($m^3\ mol^{-1}\ pa^{-1}$)	ϕ_v ($m^3 mol^{-1}$)
70	1580.392	0.886	4.5189	-18.8095	-527.4938
75	1600.824	0.885	4.4092	-19.9953	-399.5411
80	1495.304	0.887	5.0422	-12.9485	-655.1580
85	1515.760	0.885	4.9181	-14.2263	-399.5411
90	1482.120	0.884	5.1497	-11.5345	-271.2989

Table 14: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_2 Temp. = 300 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V ($m. sec^{-1}$)	ds x 10^3 ($Kg.m^{-3}$)	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} ($m^3\ mol^{-1}\ pa^{-1}$)	ϕ_v ($m^3 mol^{-1}$)
70	1568.064	0.882	4.6111	-17.5108	24.6067
75	1519.968	0.883	4.9020	-14.2642	-104.2611
80	1647.488	0.883	4.1725	-22.7270	-104.2611
85	1496.560	0.880	5.0737	-12.1157	283.2209
90	1520.360	0.881	4.9106	-14.0394	153.7670

Table 15: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_3 Temp. = 300 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V ($m. sec^{-1}$)	ds x 10^3 ($Kg.m^{-3}$)	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} ($m^3\ mol^{-1}\ pa^{-1}$)	ϕ_v ($m^3 mol^{-1}$)
70	1595.856	0.882	4.4519	-19.1099	57.4865
75	1520.432	0.884	4.8934	-14.4085	-200.0319
80	1496.960	0.881	5.0653	-12.2598	186.6841
85	1585.040	0.882	4.5129	-18.6134	57.4865
90	1481.248	0.880	5.1792	-10.8954	316.1754

Table 16: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_4 Temp. = 300 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V ($m. sec^{-1}$)	ds x 10^3 ($Kg.m^{-3}$)	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} ($m^3\ mol^{-1}\ pa^{-1}$)	ϕ_v ($m^3 mol^{-1}$)
70	1522.416	0.871	4.9535	-12.8579	1552.3825
75	1495.904	0.870	5.1366	-10.9393	1684.9319
80	1440.472	0.871	5.5331	-6.1740	1552.3825
85	1438.664	0.873	5.5344	0.2795	1288.1946
90	1340.160	0.864	6.4443	4.9352	2486.6720

Table 17: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_5 Temp. = 300 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V (m. sec^{-1})	ds x 10^3 (Kg.m^{-3})	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} (m^3 mol^{-1} pa^{-1})	ϕ_v (m^{3}mol^{-1})
70	1521.736	0.873	4.9466	-13.1067	1210.3022
75	1532.480	0.869	4.8999	-13.3843	1739.5356
80	1448.930	0.868	5.4876	-6.5230	1873.6061
85	1437.912	0.879	5.5023	-7.1493	425.4835
90	1519.208	0.874	4.9574	-13.2598	1078.7508

Table 18: Acoustic parameters at different percentages of 1,4-dioxane-water mixture

System : Ligand – L_6 Temp. = 300 K
Concentration : 0.01 M Ultrasonic Frequency : 1 MHz

% Dioxane	V (m. sec^{-1})	ds x 10^3 (Kg.m^{-3})	βs x 10^{-7} (pa^{-1})	ϕ_k x 10^{-3} (m^3 mol^{-1} pa^{-1})	ϕ_v (m^{3}mol^{-1})
70	1521.784	0.889	4.8573	-15.1100	-820.7609
75	1519.232	0.888	4.8791	-14.8118	-693.5707
80	1521.520	0.887	4.8699	-14.8536	-566.0937
85	1409.424	0.886	5.6818	-5.5903	-438.3290
90	1480.264	0.885	5.1568	-11.4740	-310.2755

Intermolecular Free Length (L_f)

L_f increases with increase in the percentage of organic solvent in dioxane-water mixture at different temperature. Ultrasonic velocity depends on intermolecular free length L_f with decrease in free length velocity increases or vice versa. L_f increases linearly with the increasing concentration of substituted pyrazolines indicates that there is significant interaction between ion and solvent molecules suggesting a structure promoting behaviour of the added solute. This may also imply that decrease in number of free ions showing the occurrence of ionic association due to strong ion-ion interactions.

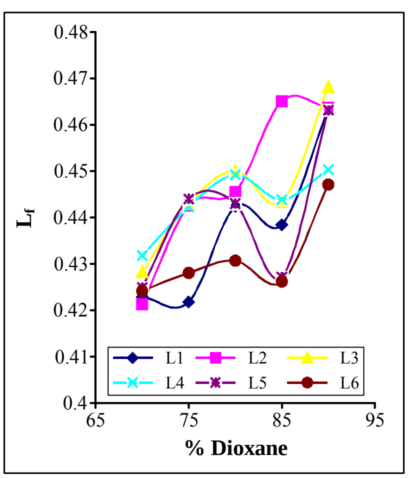

Fig. 16: Plot between % dioxane Vs L_f (Temp. 293 K)

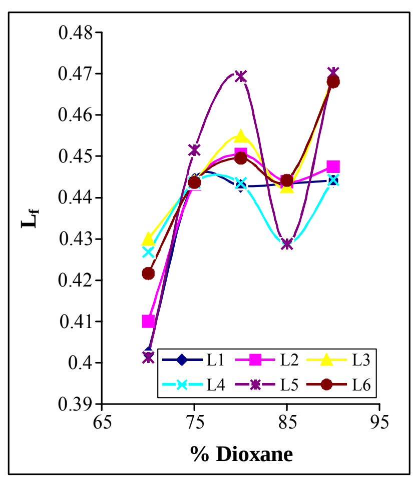

Fig. 17: Plot between % dioxane Vs L_f (Temp. 297 K)

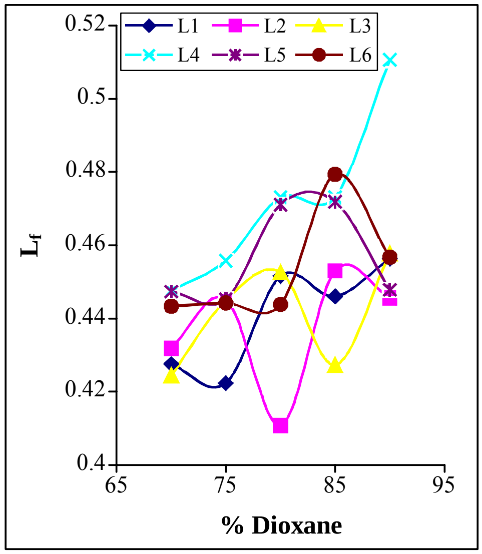

Fig. 18: Plot between % dioxane Vs L_f (Temp. 300 K)

Relative association (R_A)

Relative association is an acoustic property understanding interaction which is influenced by two opposing factors.

(i) Breaking of solvent structure on addition of solute to it, and

(ii) Solvation of the solutes that are simultaneously present by free solvent molecules.

The values of relative association (R_A) increases for all ligands L_1, L_2, L_3, L_4, L_5 and L_6 regularly with increase in the percentage of dioxane-water mixture at different temperature.

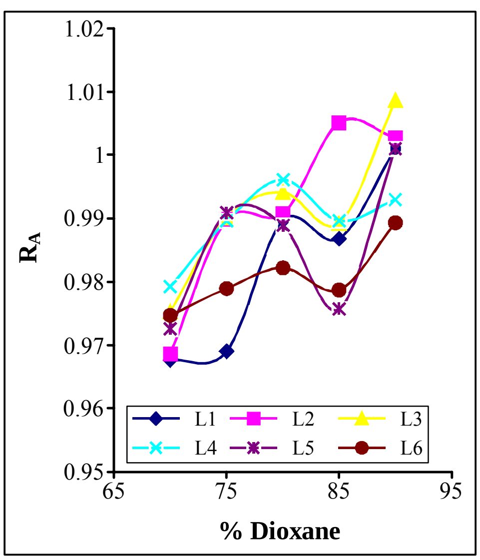

Fig. 19: Plot between % dioxane Vs R_A (Temp. 293 K)

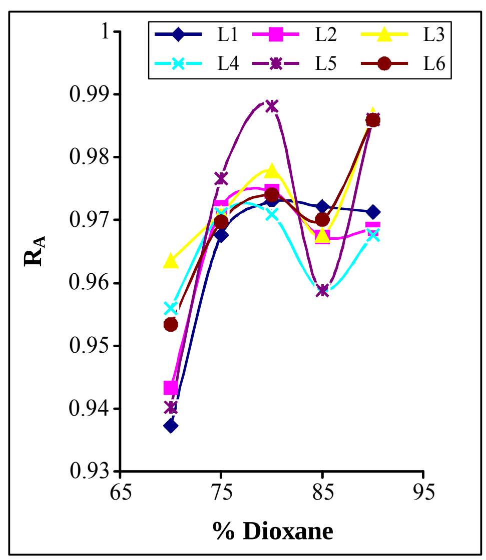

Fig. 20: Plot between % dioxane Vs R_A (Temp. 297 K)

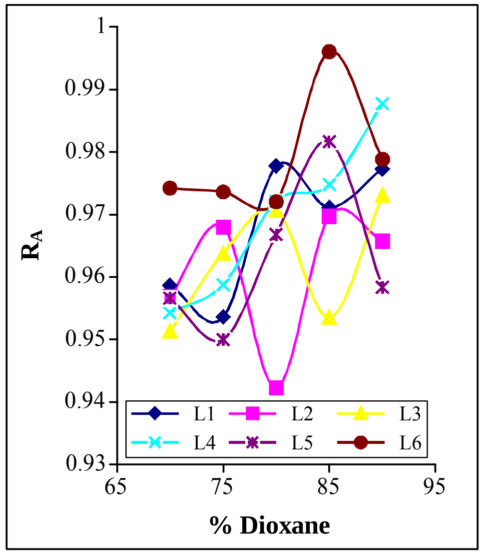

Fig. 21: Plot between % dioxane Vs R_A (Temp. 300 K)

Specific acoustic impedance (z)

The mathematical relation for specific acoustic impedance z = v.d and adiabatic compressibility $\beta = 1/v^2.d$ shows that their behaviour is opposite.

The values of specific acoustic impedance (z) of all ligand L_1, L_2, L_3, L_4, L_5 and L_6 are decreases with increase in percentage of solvent at different temperature.

From Tables, it can be seen that the values of specific acoustic impedance (z) are continuously decreasing on changing the structure of ligands. Therefore, the specific acoustic impedance depends upon the various structure of liquid and molecular packing of the medium.

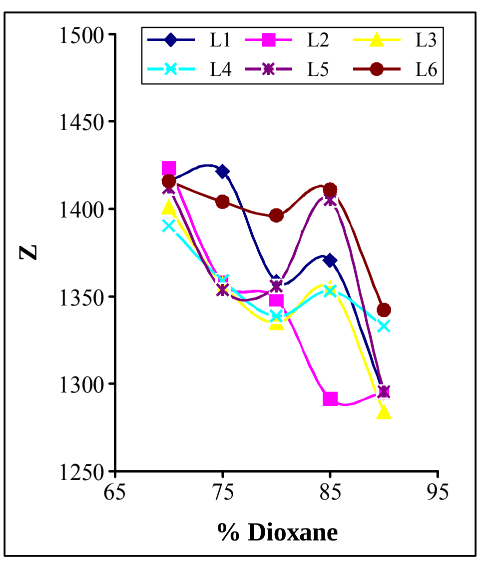

Fig. 22: Plot between % dioxane Vs Z (Temp. 293 K)

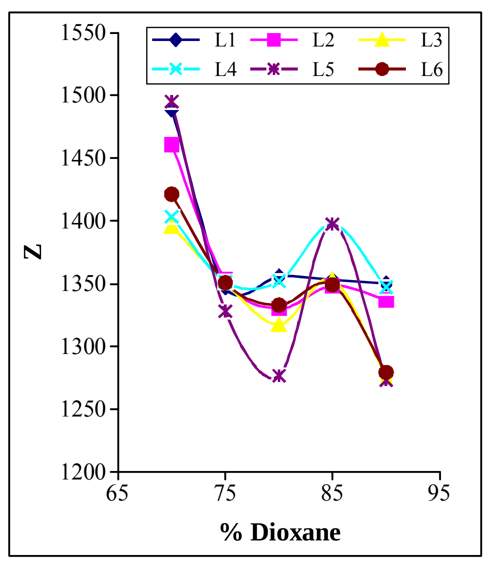

Fig. 23: Plot between % dioxane Vs Z (Temp. 297 K)

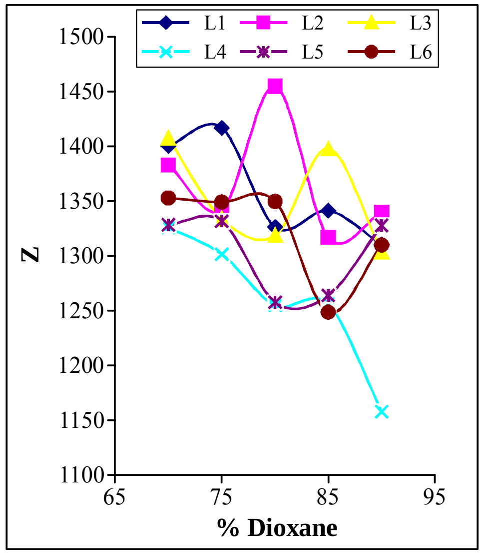

Fig. 24: Plot between % dioxane Vs Z (Temp. 300 K)

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