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Ultrasonic Interferometric Investigations of 3-(Chloroaryl)-5-aryl-1-substituted Pyrazolines in Dioxane Medium

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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 293K , 297K and 300 K . The data obtained during the study is used for determing most significant acoustic parameters like Velocity (v), Density (d), relative association (R_A),intermolecular free length (L_f), specific acoustic impedance (z). 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.
Keywords : Substituted Pyrazolines, Acoustic Parameters, Interferometry, Solute-solvent Intera.

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 30^0-40^0 c and ion solvent interaction has been inferred2. Speeds of Sound & Isentropic Compressibillities3 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.

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

1. 3-(2-Hydroxy-5-chlorophenyl)-5-phenyl-1-thiocarboxamido pyrazoline (L_1)
2. 3-(2-Hydroxy-5-chlorophenyl)-5-(3-chlorophenyl)-1-thiocarboxamido pyrazoline (L_2)
3. 3-(2-Hydroxy-3-bromo-5-chlorophenyl)-5-phenyl-1-thiocarboxamido pyrazoline (L_3)
4. 3-(2-Hydroxy-3-bromo-5-chlorophenyl)-5-(3-chlorophenyl)-1-thiocarboxa-mido pyrazoline (L_4)
5. 3-(2-Hydroxy-3-nitro-5-chlorophenyl)-5-phenyl-1-thiocarboxamido pyrazoline (L_5)
6. 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 0.01M Solutions of different percentage of dioxane solvent of L1, L2, L3, L4, L5 and L6 were determined from these R_A, L_f, z . 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[9]. The solvent 1,4-dioxane were purified by standard procedure[10]. 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 1MHz 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.293K, 297K, 300K.

Results and Discussion

A study of R_A ,L_f and z 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 ($kg.m^{-3}$)	R_A	L_f x10^{-2} (m^{-1})	Z ($kg\ m^{-2}\ sec^{-1}$)
70	1597.00	0.887	0.9676	0.4229	1416.539
75	1599.06	0.889	0.9690	0.4218	1421.5608
80	1521.31	0.893	0.9897	0.4424	1358.5298
85	1534.86	0.893	0.9868	0.4385	1370.6264
90	1454.77	0.890	1.001	0.4634	1294.7435

Table2: 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 ($kg.m^{-3}$)	R_A	L_f x10^{-2} (m^{-1})	Z ($kg\ m^{-2}\ sec^{-1}$)
70	1601.032	0.889	0.9686	0.4213	1423.3174
75	1520.72	0.893	0.9898	0.4426	1358.0030
80	1511.640	0.892	0.9907	0.4455	1348.3829
85	1447.816	0.892	1.0051	0.4651	1291.4519
90	1453.124	0.891	1.0027	0.4637	1294.7335

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 ($kg.m^{-3}$)	R_A	L_f x10^{-2} (m^{-1})	Z ($kg\ m^{-2}\ sec^{-1}$)
70	1573.984	0.890	0.9753	0.4283	1400.8458
75	1519.456	0.893	0.9901	0.4429	1356.8742
80	1496.136	0.892	0.9941	0.4501	1334.5533
85	1518.800	0.892	0.9892	0.4434	1354.7696
90	1437.600	0.893	1.0086	0.4682	1283.7768

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})	R_A	L_f x10^{-2} (m^{-1})	Z (kg m^{-2} sec^{-1})
70	1560.512	0.891	0.9792	0.4318	1390.4162
75	1521.760	0.893	0.9896	0.4423	1358.9317
80	1497.432	0.894	0.9961	0.4492	1338.7042
85	1516.880	0.892	0.9896	0.4439	1353.0570
90	1496.160	0.891	0.9930	0.4503	1333.0786

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})	R_A	L_f x10^{-2} (m^{-1})	Z (kg m^{-2} sec^{-1})
70	1586.768	0.890	0.9726	0.4249	1412.2235
75	1515.792	0.893	0.9909	0.4440	1353.6023
80	1519.960	0.892	0.9889	0.4430	1355.8043
85	1577.040	0.891	0.9757	0.4272	1405.1426
90	1455.528	0.890	1.0010	0.4632	1295.4199

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})	R_A	L_f x10^{-2}(m^{-1})	Z(kg m^{-2} sec^{-1})
70	1587.328	0.892	0.9747	0.4242	1415.8966
75	1572.288	0.893	0.9789	0.4281	1404.0532
80	1561.904	0.894	0.9822	0.4307	1396.3422
85	1578.312	0.894	0.9787	0.4262	1411.0109
90	1508.00	0.890	0.9893	0.4471	1342.1200

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})	R_A	L_f x10^{-2}(m^{-1})	Z (kg m^{-2} sec^{-1})
70	1678.600	0.887	0.9373	0.4023	1488.9182
75	1520.648	0.886	0.9676	0.4443	1347.2941
80	1521.715	0.891	0.9729	0.4428	1355.8454
85	1520.352	0.890	0.9721	0.4434	1353.1133
90	1518.720	0.889	0.9713	0.4441	1350.1421

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})	R_A	L_f x10^{-2}(m^{-1})	Z(kg m^{-2} sec^{-1})
70	1647.016	0.887	0.9433	0.4100	1460.9032
75	1520.648	0.890	0.9720	0.4433	1353.3767
80	1498.232	0.888	0.9746	0.4505	1330.4300
85	1522.080	0.886	0.9673	0.4439	1348.5629
90	1510.792	0.885	0.9686	0.4475	1337.0509

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})	R_A	L_f x10^{-2}(m^{-1})	Z(kg m^{-2} sec^{-1})
70	1566.768	0.891	0.9635	0.4300	1395.9903
75	1519.640	0.889	0.9711	0.4439	1350.9600
80	1483.736	0.888	0.9778	0.4549	1317.5576
85	1525.776	0.887	0.9676	0.4426	1353.3633
90	1438.880	0.887	0.9867	0.4693	1276.2866

Table10 : 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})	R_A	L_f x10^{-2}(m^{-1})	Z(kg m^{-2} sec^{-1})
70	1585.272	0.887	0.9560	0.4268	1403.4753
75	1520.256	0.889	0.9710	0.4437	1351.5076
80	1520.784	0.889	0.9709	0.4435	1351.9770
85	1573.832	0.888	0.9588	0.4288	1397.5628
90	1520.632	0.886	0.9676	0.4443	1347.2800

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})	R_A	L_f x10^{-2}(m^{-1})	Z(kg m^{-2} sec^{-1})
70	1680.048	0.890	0.9402	0.4013	1495.2427
75	1494.064	0.889	0.9766	0.4515	1328.2229
80	1437.896	0.888	0.9881	0.4694	1276.8516
85	1573.808	0.888	0.9588	0.4288	1397.5415
90	1437.120	0.886	0.9860	0.4702	1273.2883

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})	R_A	L_f x10^{-2}(m^{-1})	Z(kg m^{-2} sec^{-1})
70	1600.712	0.888	0.9534	0.4216	1421.4323
75	1521.128	0.888	0.9697	0.4437	1350.7617
80	1501.112	0.888	0.9740	0.4496	1332.9875
85	1519.312	0.888	0.9701	0.4442	1349.1491
90	1442.480	0.887	0.9859	0.4681	1279.4798

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})	R_A	L_f x10^{-2}(m^{-1})	Z(kg m^{-2} sec^{-1})
70	1580.392	0.886	0.9587	0.4275	1400.2273
75	1600.824	0.885	0.9536	0.4223	1416.7292
80	1495.304	0.887	0.9777	0.4516	1326.3346
85	1515.760	0.885	0.9711	0.4460	1341.4476
90	1482.120	0.884	0.9773	0.4564	1310.1941

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})	R_A	L_f x10^{-2}(m^{-1})	Z(kg m^{-2} sec^{-1})
70	1568.064	0.882	0.9569	0.4319	1383.0324
75	1519.968	0.883	0.9680	0.4453	1342.1317
80	1647.488	0.883	0.9423	0.4108	1454.7319
85	1496.560	0.880	0.9697	0.4530	1316.9728
90	1520.360	0.881	0.9657	0.4457	1339.4372

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})	R_A	L_f x10^{-2}(m^{-1})	Z(kg m^{-2} sec^{-1})
70	1595.856	0.882	0.9513	0.4244	1407.5450
75	1520.432	0.884	1.0438	0.4449	1334.0619
80	1496.960	0.881	0.9707	0.4526	1318.8218
85	1585.040	0.882	0.9535	0.4273	1398.0053
90	1481.248	0.880	0.9730	0.4577	1303.4982

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})	R_A	L_f x10^{-2}(m^{-1})	Z(kg m^{-2} sec^{-1})
70	1522.416	0.871	0.9543	0.4476	1326.0243
75	1495.904	0.870	0.9588	0.4558	1301.4365
80	1440.472	0.871	0.9721	0.4731	1254.6511
85	1438.664	0.873	0.9747	0.4731	1255.9537
90	1340.160	0.864	0.9877	0.5106	1157.8982

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})	R_A	L_f x10^{-2}(m^{-1})	Z(kg m^{-2} sec^{-1})
70	1521.736	0.873	0.9566	0.4473	1328.4755
75	1532.480	0.869	0.9500	0.4452	1331.7251
80	1448.930	0.868	0.9668	0.4711	1257.6712
85	1437.912	0.879	0.9816	0.4718	1263.9246
90	1519.208	0.874	0.9583	0.4478	1327.7878

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})	R_A	L_f x10^{-2}(m^{-1})	Z(kg m^{-2} sec^{-1})
70	1521.784	0.889	0.9742	0.4433	1352.8660
75	1519.232	0.888	0.9736	0.4442	1349.0780
80	1521.520	0.887	0.9720	0.4438	1349.5882
85	1409.424	0.886	0.9960	0.4794	1248.7497
90	1480.264	0.885	0.9788	0.4567	1310.0336

Relative Association (R_A)

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

1. Breaking of solvent structure on addition of solute to it[7], and
2. 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.

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 is 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.

Specific Acoustic Impedance (z)

The mathematical relation for specific acoustic impedance z = v.d and adiabatic compressibility □ = $1/v^2$.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. 19
Plot between % dioxane Vs R_A
Temp. 293 K

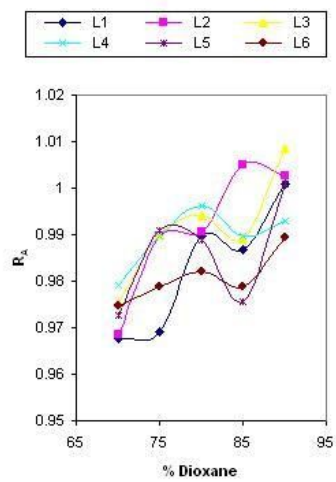


Fig. 20
Plot between % dioxane Vs R_A
Temp. 297 K

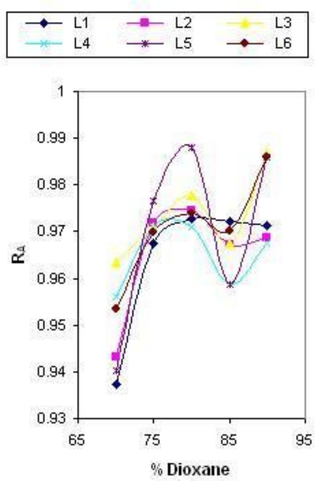


Fig. 21
Plot between % dioxane Vs R_A
Temp. 300 K

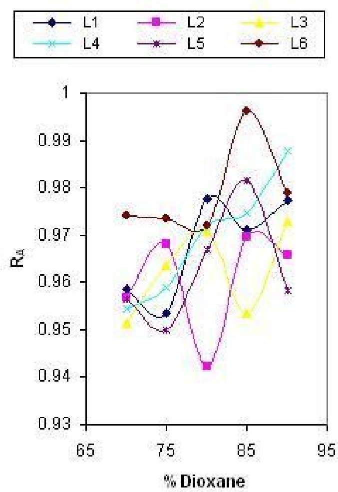


Fig. 16
Plot between % dioxane Vs L_f
Temp. 293 K

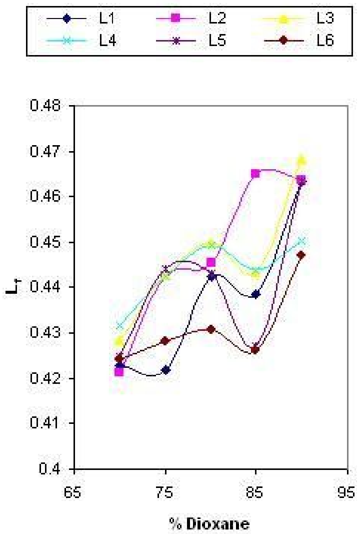


Fig. 17
Plot between % dioxane Vs L_f
Temp. 297 K

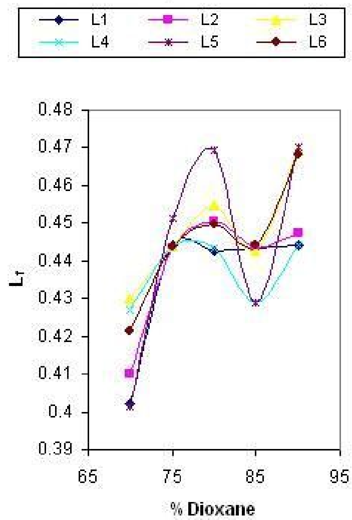


Fig. 18
Plot between % dioxane Vs L_f
Temp. 300 K

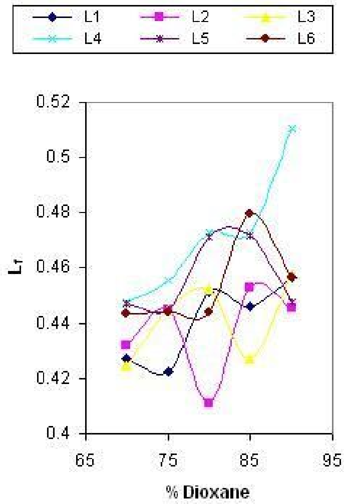


Fig. 22
Plot between % dioxane Vs Z
Temp. 293 K

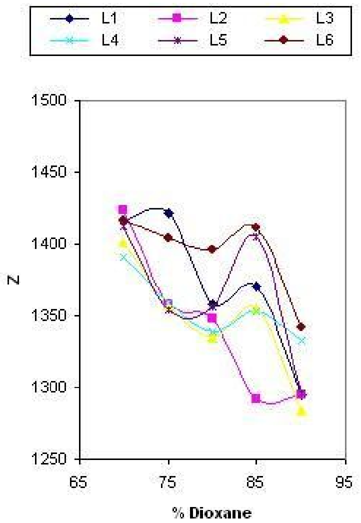


Fig. 23
Plot between % dioxane Vs Z
Temp. 297 K

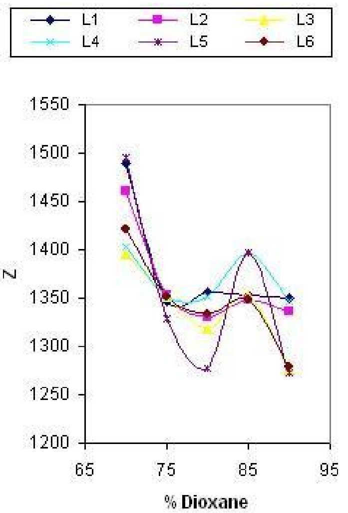
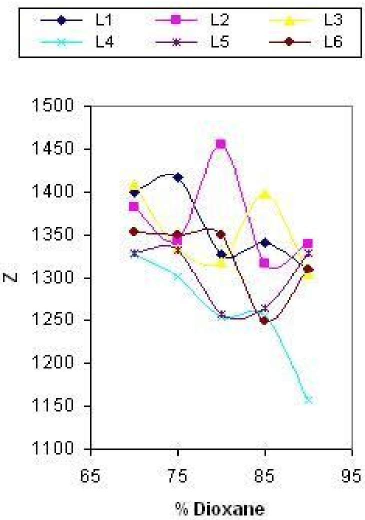


Fig. 24
Plot between % dioxane Vs Z
Temp. 300 K



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