



**STUDIES IN STABILITY CONSTANTS, VISCOSITY AND REFRACTIVITY INDEX OF CU(II), CO(II) AND NI(II) COMPLEXES WITH 1-(3-BROMO-2-HYDROXY-5-METHYLPHENYL)-3-PHENYLPROPANE-1,3-DIONE (L) AT 0.1M STRENGTH**

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**ABSTRACT**

The physical parameters like viscosity and stability constant in 70% dioxane-Water and refractive index and polarizability constant in different concentration with 1-(3-bromo-2-hydroxy-5-methylphenyl)-3-phenylpropane-1,3-dione (L) at 305.15<sup>0</sup>K. Favourable results are obtained of stability constants. By using Calvin Bjerrum Irving-Rassoti's method the stability constants of complex formation have been studied, titration is done in an inert atmosphere at 0.1M ionic strength and temp. (305.15<sup>0</sup>K) pH metrically. The measurements of refractive index are done by Abbe's refractometer. In the present investigation, molar refractivity and polarizability constants of ligands solution have been studied. It is found that molar refractivity and polarizability constants are decrease with increase in density of solution.

**Key Words:** pH metric study, stability constant, refractivity and polarizability

**INTRODUCTION**

The viscosity is one of the important physical parameter of liquids which provides valuable information with respect to solute-solute and solvent-solvent interaction in aqueous and non-aqueous solution<sup>1-5</sup>. Molecular interactions of mixture is also studied by many workers<sup>6-12</sup>. The Jones-Doles<sup>13</sup> equation for the accounts of viscosity concentration dependence of dilute electrolyte solutions while Breslau Miler<sup>14</sup> and Vand<sup>15</sup> account for the concentration dependence of viscosity in concentrated electrolyte solution. Berry and Irving<sup>16</sup> have determined viscosities of concentrated aqueous electrolyte solution at various concentrations. Narwade et al<sup>17</sup> have



presented the metal ligand stability constant of  $UO_2$  (II) and Cu (II) complexes with some substituted sulphonic acids. Agrawal et al<sup>18</sup> have studied the metal ligand stability constant of Fe(II), Cr(III) and Al(III) metal ions with some substituted pyrazoles and studied viscosity of some substituted flavones, isooxazole and pyrazoles in 70% acetone water mixture. Recently some workers presented the measurement of viscosity, refractivity index and metal -ligand stability constant of substituted ligands of binary complexes by pH metrically. After literature survey it is observed that study viscosity of, refractive index and stability constant have not been reported. So we have selected this scheme for this paper.

## EXPERIMENTAL SECTION

**Chemicals:** All chemicals are analytical reagent (AR) grade with were obtained from Sd Fine chemicals, India which is used as such without further purification. The Cu (II), Ni (II) and Co (II) metal ions and complexes dissolving it in proper solvent.

**Ligand:** In present investigation the ligand was synthesized in laboratory by standard methods for studying it was checked by M.P, TLC, and structure was established on the basis of elemental analysis, IR and NMR data.

**Viscosity:** The viscosities were measured by using Oswald's viscometer, which was kept in thermostatic water bath ( $\pm 0.10^\circ\text{C}$ ) and maintaining each measurement sufficient time was allowed to maintain the constant temp.

**Refractive index:** By using Abbe's refractometer the refractive indices of ligands solution were determined.

**Stability constants:** Metal ligand stability constants of metal complexes are carried out at 0.1 ionic strength in 70% dioxane-water mixture using Bjerrum titration Process.

## RESULT AND DISCUSSION

By using Irving-Rassoti's equation proton ligand stability constant are evaluated by half integral method and pointwise calculation method which are given below table.



**Table -I. Proton Ligand Stability Constant**

System	Half integral method	Point wise calculation method
L-Co(II)	8.20	8.31±0.05
L-Cu(II)	9.80	9.75±0.02
L-Ni(II)	8.60	8.70±0.04

From the above table -I Pk, values of system L-Ni(II) is lesser than pKa values of systems L-Cu(II) and L-Co(II), The change in colors with respect pH during titration process and the deviation between ligand curve and ligand+acid curve also indicate the complex formation Logk<sub>1</sub> (metal ligand stability constant for 1:1 complex) and Logk<sub>2</sub> (metal ligand stability constant for 1:2 complex) or evaluated using Irving Rassotti's expression which are presented in table -II.

**Table -II. Metal Ligand Stability Constant**

System	Pk <sub>1</sub>	Pk <sub>2</sub>
L-Co(II)	7.14362	5.7532
L-Cu(II)	8.9553	7.3642
L-Ni(II)	5.8543	4.8635

The relative viscosities have been analysed by Jones-Dole equation<sup>73</sup>.

$$(\eta_r - 1) / \sqrt{C} = A + B \sqrt{C} \quad \text{..... (3)}$$

where, C is molar concentration of the ligand solution, A is the viscosity coefficient which measures solute-solute interaction and B is viscosity coefficient which measure solute-solvent interaction. The graphs are plotted between  $(\eta_r - 1) / \sqrt{C}$  Vs  $\sqrt{C}$ . The graph for each system gives linear straight line showing validity of Jones-Dole equation. The slope of straight line gives value of B-coefficient. In the present study, relative viscosity of ligand solutions increases with



increase in the concentration of ligand. The increase in viscosity with increase in concentration may be attributed to the increase in solute–solvent interactions. The plots of  $(\eta_r - 1) / \sqrt{C}$  Vs  $\sqrt{C}$ , gives positive B-coefficient values which indicates the presence of solute-solvent interactions. The values of viscosity ( $\eta$ ) and relative viscosity ( $\eta_r$ ) of system in 70% of dioxane-water mixtures are represented in at difference concentrations are represented in TableIII.

**Table -III: Measurement of Viscosity.**

Temp. :  $305.15 \pm 0.01^\circ\text{k}$

medium: 70% dioxane-Water

Conc. Mole $\text{dm}^{-3}$	$\sqrt{C}$ $\text{Mole}^{-1/2} \text{dm}^{-3/2}$	Density ( $\rho$ ) $\text{g.cm}^{-3}$	Time Flow Sec	Viscosity Cp	Relative Viscosity	Specific Viscosity $\eta_{\text{Sp}}$ $= \eta_r - 1/\sqrt{C}$
0.010	0.1301	1.04313	97.9	1.11761	1.6236	1.6476
0.008	0.1970	0.04320	95.9	1.09488	1.5997	1.5142
0.006	0.09746	0.04341	94.2	1.07664	1.58069	1.37211
0.004	0.09326	1.0456	91.8	1.05071	1.5532	1.19481
0.002	0.07471	1.0469	90.0	1.0181	1.51901	0.7141

The molar refraction of compound is determined as,

$$R_{\text{ligand}} = R_{\text{mixture}} - R_{\text{Dioxane-Water}}$$

Where,

$R_{\text{Dioxane-Water}}$  - The molar refraction of solvent, Dioxane-Water mixture. The molar refractivity of complexes was determined using formula  $R_M = n^2 - 1 / n^2 + 2 \times M/d$

$$R_M = 4/3 \pi N_0 \alpha$$



**Table - IV - Molar Refraction and Polarizability Constant at Different Concentrations for 70% of Dioxane-Water Mixture**

Ligand	Concentration (M)	Density Kg.cm <sup>-1</sup>	Refractive index ( $\eta$ )	R <sub>mixture</sub> (cm <sup>3</sup> .mole <sup>-1</sup> )	R <sub>Ligand</sub> (cm <sup>3</sup> .mole <sup>-1</sup> )	$\alpha \times 10^{-23}$ (cm <sup>3</sup> )
L	0.1005	1.0241	1.4107	8.8432	0.7881	0.03126
	0.0755	1.0239	1.4087	8.7600	0.7050	0.02799
	0.0565	1.0236	1.4075	8.7034	0.6483	0.02572
	0.0425	1.0233	1.4057	8.6390	0.5834	0.02312

After observing the above tables it can be suggested that, at 305.15°k the temperature of mixture, the molar refractivity and polarizability constant continuously increases with concentration. The higher apparent molar compressibility value in dioxane solvent making the solution more compressible.

Due to the fact that at this temperature of dioxane, there is increase in dielectric constant of medium with concentration. The polar solute have acquires a partial positive charge on hydrogen atom; there are weak interactions between this positive charge and negative charge on oxygen atom (electronegativity) of dioxane. The weak interaction of the wonder wall's forces is in the solution i.e. specific arrangement of dioxane molecule may be occurring due to attached solute molecule.

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