

Co(II) and Ni(II) Complexes of Some Substituted Pyrazoles and Diketones at 0.1M Strength: Metal-Ligand Stability Constants, Viscosity, Refractivity Index Studies

G. B. Pethe, U. P. Meshram

Department of Chemistry, Narayanrao Kale Smruti Model College (Arts, Comm. and Science)
Karanja Ghadge, Dist.-Wardha, M.S., India
E mail-gaurav.pethe@gmail.com

Abstract:

The physical properties such as viscosity and metal-bonding stability constant in 70% DMSO-Water and refractive index and polarizability constant in different concentration with pyrazoles and diketones at 30°C. The results obtained of stability constant are in good agreement. Measurements of refractive index have been studied by Abbe's refractometer. Molar refractivity and polarizability constants of ligands solution have been evaluated in the present investigation. It could be seen that molar refractivity and polarizability constants are found to be decreased with increase in density of solution. The stability constants of metal-ligand complex formation of Co(II) and Ni(II) with pyrazoles and diketones have been studied using Irving-Rassot's Method and titration is done by using Calvin Bjerrum Method in an inert atmosphere at 0.1M ionic strength and temp. (30°C ± 0.1°C) pH metrically.

Keywords: Substituted Pyrazoles and Diketones, Molar Refractivity and Polarizability constant, metal-bonding stability constant, DMSO.

Introduction:

Coordination compounds play many important roles in animals and plants, their chemical and biological processes [1-3], chlorophyll is one of the most important chelates in nature; it is essential to photosynthesis in plants and one important porphyrin chelate is heme, the central component of hemoglobin, which carries oxygen through blood in animal cells, is an iron complex, coenzyme vit-B₁₂ which serves as a prosthetic group. Studies on enzymes have shown that the site of reaction in biological systems is frequently a complex metal ion. Most of the industrial processes depend directly on catalysis by metal complexes. Many workers studied the effect of solute-solvent interaction on protonation equilibria of organic acids and chelation equilibria of their transition metal ion complexes. The study of complexes of Cu(II), Ni(II) and Co(II) with HMAPTST [4] has been investigated pH metrically. Gudadhe et al [5] have studied the proton-ligand and metal ligand stability constants of Th(V) complexes with some substituted pyrazolines at 0.1M ionic strength in 70% dioxane-water mixture. Taha et al [6, 7] have discussed that stability of ternary complexes in relation to that of binary complexes with bicine and tricine and the evaluated effect of temperature and ionic strength of the medium on the system, stability constants and thermodynamic parameters (ΔG , ΔH and ΔS) of complexes of glutathione with Cu(II), Pb(II), Ni(II) and Zn(II). Catharina et al [8] have reported lanthanide complexes with unsubstituted pyrazolate and Cp-analogous pyrazole spectrophotoelectrically $n-\sigma$ and $n-\pi$ bending modes. From the literature survey it is observed that study viscosity, refractive index and stability constants of Co(II) and Ni(II) ion with L_1 (BPBHPP), L_2 (CPBHPP), L_3 (HPPCPD) and L_4 (HPMBPD) have not been reported. Therefore we have selected this work for research purpose. In present investigation viscosity study of

L₃(HPPCPD) at 30°C have been carried out and metal ligand stability constant of L₁ (BPBHPP), L₂(CPBHPP), L₃(HPPCPD) and L₄(HPMBPD) in 70% DMSO solvent-water also studied. Refractive index of L₁ (BPBHPP), L₂(CPBHPP), L₃(HPPCPD) and L₄(HPMBPD) in DMSO solvent was reported.

Experimental:

The Heterocyclic ligands L₁, L₂, L₃ and L₄(fig. 1) are used in the present investigation are synthesized by the known standard literature methods [9, 10] for studying its physical properties in the present work, its purity was checked by M.P and TLC and structure was established on the basis of elemental analysis, IR and NMR data. DMSO solvent and chemicals used were of AR grade from SD fines Chemicals and conductivity water was used. The densities of the ligand solutions and solvents were determined by standard methods. The viscosities were measured by the means of Oswald's viscometer ($\pm 0.11\%$ $\text{kgm}^{-1}\text{s}^{-1}$), which was kept in equilibrium with thermostatic water bath ($\pm 0.1^\circ\text{C}$). For each measurement sufficient time was allowed to maintain the constant temperature by attaining thermal equilibrium in a thermostat. The refractive index of ligands solution were determined by using Abbe's refractometer, the accuracy of the instruments was ± 0.001 unit; ligands solution was prepared in DMSO solvent. For determination of metal ligand stability constants of Co(II) and Ni(II)- L₁, L₂, L₃ and L₄ complexes p^H metrically, three titrations, acids titration, ligand titration and metal titration are carried out at 0.1 ionic strength in 70% DMSO-water mixture using Bjerrium titration Process [11].

Results and Discussion:

Proton ligand stability constant (p^k) or (logK^H) are evaluated by half integral method and point wise calculation method using Irving Rassoti's expressions [12]. The values of p^k or logK^H obtained are presented as shown in table no. 1. It could be seen that from the results of p^k, values of ligand L₄ is lesser than pKa values of ligand L₃, this may be due to the fact of phenyl ring is very away from hydroxyl groups as compare to bulky phenyl group with ligand L₄ The value of pKa is less for ligand L₁ than L₂ may be due to the effect of bromo substituent as an electron withdrawing group.

The deviation between ligand curve and ligand+acid curve indicates that commencement of complex formation. The change in colors with respect pH during titration process also indicate the complex formation LogK₁ (metal ligand stability constant for 1:1 complex) and LogK₂ (metal ligand stability constant for 1:2 complex) or evaluated using Irving Rassotti's expression which are presented in table no. 2. The relative viscosity of each solution is determined by using empirical formula.

$$\eta_r = \eta_l / \eta_w$$

The physical properties of liquids, binary liquids, and ternary liquids mixture have been subject of interest of research work. The change structure of solvent or solution as a result of hydrogen bond formation or increase in interaction. Hydrophobic (structure making) or hydrophilic (structure breaking) character of solute i.e. hydrogen bond forming or disrupting properties can be correlated with changes in density or viscosity. Solutes can occupy the interstitial space in solvent.

The relative viscosity data of β -coefficient values responsible for solute solvent interaction in different concentration of L₃-DMSO solvent are tabulated in table no. 3 it can be seen due to the fact of addition of more and more amount of bulky solvent i.e. DMSO that results to increase in the molecular interaction between solute and

ligand particular. The β -coefficient value is found to be very greater i.e. 79.18×10^{-08} that show stronger attraction between solute and solvent. The molar refractivity of ligands L_1 , L_2 , L_3 and L_4 in DMSO solvent was determined using formula $R_M = 4/3\pi N_0 \alpha$. The values of molar refractivity and polarizability constant of ligands L_1 , L_2 , L_3 and L_4 in DMSO solvents are reported in table no. 4

Conclusions:

It is observed that from the table no. 2 that $\text{Log}K_1$ and $\text{Log}K_2$ values for $\text{Co(II)-}L_4$ and $\text{Ni(II)-}L_4$ complexes are found to be less as compare to $\text{Log}K_1$ and $\text{Log}K_2$ values of L_1 , L_2 and L_3 -Cu (II) and Ni(II) complexes. This may be due the fact of involvement of more saturation in diketone (L_4). It could be seen that relative viscosity increases with decreases in concentration ligands solution. Slope value (β -coefficient) from graph between η_{sp}/\sqrt{c} and \sqrt{c} (fig. 2) is found out to be high i.e. 79.18×10^{-08} . It showed that there is strong interaction between solute and solvent. It observed that from table no. 4 the molar polarizability constant and molar refractivity increases with increase in molecular weight. Moreover the molar polarizability (α) is found to be in decreasing order with decrease in the molecular weight of the ligands. The greater polarizability constant of the ligands showed more planer substance possessing some dipole moment. Low value of polarizability constant of the ligands in DMSO solvent is due to effect of decreasing the polar nature of solvent.

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Table no. 1: Proton Ligand stability constants

S.N	Ligand	p^k Half integral method	p^k Point wise calculation method
1	L_1	7.10	7.21 ± 0.05
2	L_2	8.70	8.65 ± 0.02

3	L ₃	7.50	7.60±0.04
4	L ₄	7.22	7.12±0.03

Table no. 2: Metal Ligand Stability constants

S.N	Metal-Ligand system	LogK ₁	LogK ₂
1	Co(II)-L ₁	6.14363	4.7533
2	Co(II)-L ₂	7.9454	6.3543
3	Co(II)-L ₃	4.8444	3.8536
4	Co(II)-L ₄	3.3423	2.3137
5	Ni(II)-L ₁	5.4636	3.4924
6	Ni(II)-L ₂	6.2985	4.2094
7	Ni(II)-L ₃	3.8352	2.1046
8	Ni(II)-L ₄	2.1754	2.0094

Table 3: Effect of concentration on relative viscosity

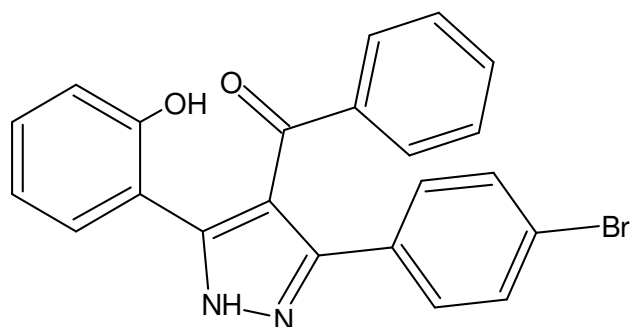
S.N	Concentration (M)	Time (S)	Density at 30°C	Viscosity (poise)	$\eta_r = \frac{\eta_l}{\eta_w}$	$\eta_{sp} = \frac{\eta_r - 1}{c}$	η_{sp}/\sqrt{c}	\sqrt{c}
1	DMSO	392	0.084	0.00720	-	-	-	-
2	0.01	483	1.002	0.1081	13.281	11.91	172.59	0.103
3	0.005	491	1.029	0.1081	13.781	12.92	126.22	0.094
4	0.0025	439	1.034	0.1094	13.984	14.18	193.83	0.042
5	0.00125	490	1.010	0.1019	13.910	11.08	491.71	0.083

Table 4: Molar refractivity's and polarizability constant of ligands in DMSO solvent

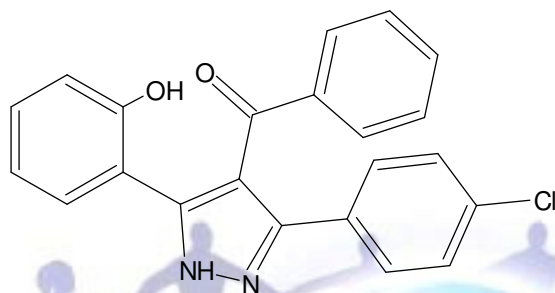
S.N	Solution	Density (Poise)	n	n ²	R _M	α
1	DMSO	0.084	-	-	-	-
2	L ₁	1.02	1.39	1.93	95.58	3.91× 10 ⁻²³
3	L ₂	1.04	1.40	1.96	89.92	3.83× 10 ⁻²³
4	L ₃	1.12	1.42	2.01	89.10	3.59× 10 ⁻²³
5	L ₄	1.09	1.47	2.16	71.95	2.39× 10 ⁻²³

Table 5: List of Abbreviations and symbols

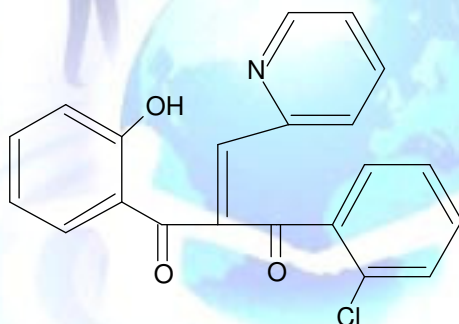
Symbol	Name
PBHPP	3(4'-bromophenyl)-4-benzoyl 5(2-hydroxyphenyl) pyrazole
CPBHPP	3(4'-chlorophenyl)-4-benzoyl 5(2-hydroxyphenyl) pyrazole
HPPCPD	1(2'-hydroxyphenyl)-2(2''-pyridylidene) 3(2'-chlorophenyl) 1,3 dione
HPMBPD	1(2'-hydroxyphenyl)-2(4''-methoxybenzylidene) 3-phenyl 1,3 dione
η _l	Viscosity of liquid
η _w	Viscosity of water
η _{sp}	Specific Viscosity
η _r	Relative Viscosity
n	Refractive Index
R _M	Molar Refraction
d	Density of solution
M	Molecular weight of ligand
No	Avogadro's number
A	Polarizability constant



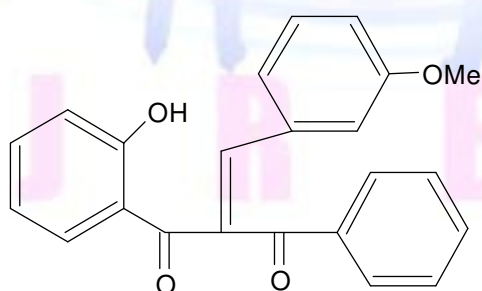
[3-(4-bromophenyl)-5-(2-hydroxyphenyl)-1H-pyrazol-4-yl](phenyl)methanone



[3-(4-chlorophenyl)-5-(2-hydroxyphenyl)-1H-pyrazol-4-yl](phenyl)methanone



(2Z)-1-(2-chlorophenyl)-3-(2-hydroxyphenyl)-2-(pyridin-2-ylmethylene)propane-1,3-dione



(2E)-1-(2-hydroxyphenyl)-2-(3-methoxybenzylidene)-3-phenylpropane-1,3-dione

Figure 1: Ligand Structures (L₁, L₂, L₃ and L₄)

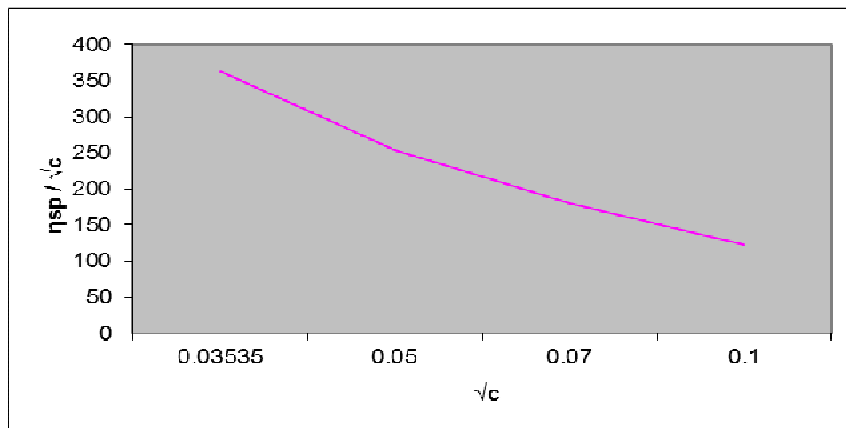


Figure 2: Graph between \sqrt{c} Vs n_{sp}/\sqrt{c}

