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Studies in Metal-ligand Stability Constants of Cu(II) Complexes and Measurement of Viscosity, Refractivity Index with some substituted Pyrazoles and Diketones at 0.1M Strength

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ABSTRACT

The interaction of metal ions with pyrazoles and diketons gained much interest as these compounds have importance in antidiabetiec drugs. The physical properties such as viscosity and metal-bonding stability constant in 70% DMSO-Water and refractive index and polarazibility constant in different concentration with diketones at 30^0c. The result obtained of stability constants are in good agreement. Mesurement of refractive index has also been studied by Abbe's refractometer. Molar refractivity and Polarazibility constants of ligands solution have been evaluated in the present investigation. It could be seen that Molar Refractivity and Polarazibity constants are found to be decreased with increase in density of solution. The stability constants of metal-ligand complex formation of Cu(II) with pyrazoles and diketones have been studied using Irving Rassoti's Method and titration is done by using Calvin Bjerrum Method in an inert atmosphere at 0.1M ionic strength and temp.(30^0c$\pm 0.1^0$c) P^H metrically.

Key Words: Substituted Pyrazoles, Diketones, p^H metry study

INTRODUCTION

The viscosity is one of the important physical properties of liquids and it implies resistance to flow. The Viscosity measurements like other transport properties of electrolytes, provides useful

information about solute-solute and solvant-solvant interaction in non aqueous and aqueous solution[1-5], molecular interactions of binary mixture are also studied by many workers[6-9], molecules interaction of electrolytes in binary mixture of two liquids have been studied by Mehrotra et al[10], Das et al[11] and Kapadi et al[12] .The Jones-Doles[13] equation accounts for the observed viscosity concentration dependence of dilute electrolyte solutions while Breslau Miler[14] and Vand[15] account for the concentration dependence of viscosity in concentrated electrolyte solution. Berry and Irvings[16] have determined viscosities of concentrated aqueous electrolyte solution at various concentrations. Pandey and Yasmin[17]have measured viscosities and densities of aqueous binary electrolyte solution of different molarities. Many attempts have been model to study viscosities of binary mixtures but no satisfactory result seems to have been obtained especially for ligands systems showings appreciable departure from ideal behaviour[18]. The properties of liquids such as viscosity, refractivity index, and ultrasonic velocity of binary mixture were studied by many workers[19-20].

Oswal et al[21] have studied dielectric constants and refractive indices of binary mixtures. Oswal et al[21]and Narwade et al[22] have investigated the metal ligand stability constant of UO_2(II) and Cu (II) complexes with some substituted sulphonic acids. Agrawal et al[23] have evaluated metal ligand stability constant of Fe(II), Cr(III) and Al(III) metal ions with some substituted pyrazoles and studied ultrasonic and viscosity of some substituted flavones, isooxazole and pyrazoles in 70% acetone water mixture.

Dadhichi et al[25] have investigated the measurement of viscosity, refractivity index and metal ligand stability constant of substituted benzofurones in different solvents. Raffique et al[26] have studied the stability constants of binary complexes with peptides by P^H metrically.

From the literature survey it is observed that study viscosity of L_4-HPMBPD, refractive index of L_1-BPBHPP, L_2-CPBHPP, L_3-HPPCPD, L_4-HPMBPD and stability constant of Cu(II) with pyrazoles (L_1-BPBHPP and L_2-CPBHPP) and diketones L_3-HPPCPD) have not been reported. Therefore we have selected this work for research purpose. The present work deals with study viscosity behavior of L_4-HPMBPD at different concentration have been reported at 30^0c and metal ligand stability constant of L_1, L_2, L_3 in 70% DMSO solvent-water and refractive index of L_1, L_2, L_3, and L_4 in DMSO solvent.

EXPERIMENTAL SECTION

Heterocycles containing pyrazoles nuclei has been reported to have biological activities like antidiuretic, antihelmentic activity in addition to fungal activity[24], antienzymatic, hypolipidermic, antidiabetics etc. Very recently substituted pyrazoles are found to be excellent antifungal agents. In the view of many analytical applications and use as a antibiotic drug in pharmaceutical and chelating. The ligands pyrazoles BPBHPP, CPBHPP and diketones HPMBPD, HPMBPD used in present investigation was synthesized in our laboratory by standard methods for studying its physical properties in the present work its purity was checked by M.P, TLC, and structure was established on the basis of elemental analysis, IR and NMR data.

DMSO solvent and chemicals used were of AR grade 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 ±0.11% $gm^{-1}s^{-1}$), which was kept in equilibrium with thermostatic water bath ($\pm 0.1^0$c). For each measurement sufficient time was allowed to maintain the constant temp. By attaining thermal equilibrium in a thermostat. The refractive indices of ligands solution were determined by using Abbe's refractometer, the accuracy of the instruments was ± 0.001unit; ligands solution was prepared in DMSO solvent.

For determination of metal ligand stability constants of Cu(II)- L_1, L2, L3 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.

RESULT 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. The values of P^k or $Logk^H$ obtained are presented as shown in table 1

Table 1. Proton Ligand Stability Constant

System	P^k Half integral method	P^k Point wise calculation method
Ligand L_1-BPBHPP	7.10	7.21±0.05
Ligand L_2-CPBHPP	8.70	8.65±0.02
Ligand L_3-HPPCPD	7.50	7.60±0.04

It could be seen that from the table1 P^k, values of ligand L_3 (diketone) is lesser than p^{Ka} values of ligand L_2, this may be due to the fact of phenyl ring is very away from hydroxyl groups as compare to bulky phenyl group with ligand L_2 The value of p^{Ka} is less for ligand L_1 may be due to the effect of bromo substituent as a 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 $Logk_1$ (metal ligand stability constant for 1:1 complex) and $Logk_2$ (metal ligand stability constant for 1:2 complex) or evaluated using Irving Rassotti's expression which are presented in table 2

Table 2 Metal Ligand Stability Constant

System	$Logk_1(Logk_{L1})$	$Logk_2(Logk_{L2})$
Cu(II)-L_1	6.14363	4.7533
Cu(II)-L_2	7.9454	6.3543
Cu(II)-L_3	4.8444	3.8536

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 inertial space in solvent.

The relative viscosity data of β-coefficient values responsible for solute solvent interaction in different concentration of L_4 DMSO solvent are tabulated in table 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 values is found to be very greater i.e. 366.0×10^{-1} that show stronger attraction between solute and solvent

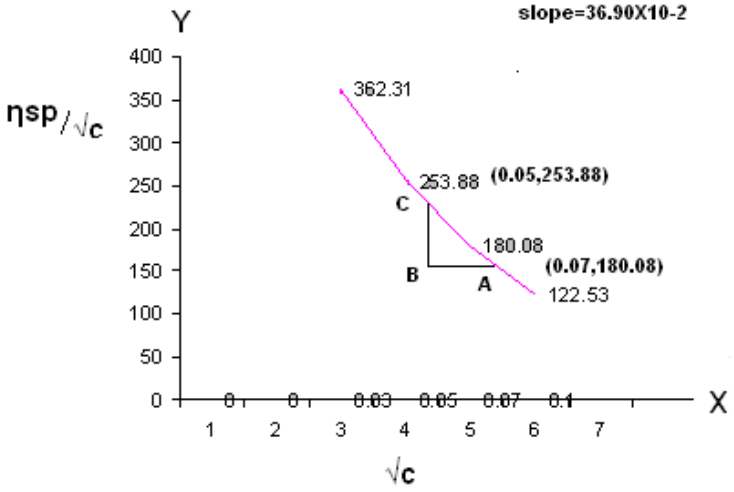

Figure no.1 between $\sqrt{c}$ Vs $\eta_{sp} / \sqrt{c}$

Table3. Effect of Concentration on Relative Viscosity

Concentration (M)	Time (Sec)	Density at 30^0c	Viscosity (Poise)	$\eta_r = \eta_l / \eta_w$	$\eta_{sp} = \eta_{r-1}$	$\eta_{sp} / \sqrt{c}$	$\sqrt{c}$
DMSO	396	0.0891	0.00793	-	-	-	-
0.01	467	1.001	0.1051	13.253	12.253	122.53	0.100
0.005	478	1.0034	0.1079	13.606	12.606	180.08	0.070
0.0025	481	1.0037	0.1086	13.694	12.694	253.88	0.050
0.00125	485	1.0041	0.1095	13.808	12.808	362.31	0.03535

The molar refractivity of ligands L_1, L_2, L_3, and L_4 in DMSO solvent was determined using formula

$$R_M = n^2 - 1 / n^2 + 2 \times M/d$$
$$R_M = 4/3\pi N o \alpha$$

The values of molar refractivity and polarizibility constant of ligands L_1, L_2, L_3, and L_4 in DMSO solvents are reported in table 4

Table4. Molar Refractivity's and Polarazibility Constant of ligands in DMSO solvent

Solution	**Density (Poise)**	***n***	n^2	R_M	**α**
DMSO	0.0891	-	-	-	-
L_1	1.001	1.3730	1.8851	95.38	3.781×10^{-23}
L_2	1.001	1.3935	1.9410	89.33	3.542×10^{-23}
L_3	1.001	1.4050	1.9740	89.003	3.529×10^{-23}
L_4	1.001	1.3225	1.7490	71.45	2.833×10^{-23}

CONCLUSION

It is observed that from the table 2 that $Logk_1$ and $Logk_2$ values for Cu(II)-L_3 complexes are found to be less as compare to $Logk_1$ and $Logk_2$ values of Cu(II)-L_1 and Cu(II)-L_2 complexes. This may be due the fact of involvement of more saturation in diketones.

It could be seen that relative viscosity increases with decreases in concentration ligands solution. Slope value (β-coefficient) from fig.1 between $\eta_{sp} / \sqrt{c}$ and $\sqrt{c}$ is found out to be high i.e. 36.90×10^{-2}.It showed that there is strong interaction between solute and solvent.

It observed that from table 4 the Molar Polarizibility constant and Molar refractivity increases with increase in molecular weight. Morever the Molar Polarizibility (α) is found to be in decreasing order with decrease in the molecular weight of the ligands. The greater polarizibility constant of the ligands showed more planer substance possessing some dipole moment. Low value of polarizibility constant of the ligands in DMSO solvent is due to effect of decreasing the polar nature of solvent.

Table5. List of Abbreviations and symbols

S.N.	Symbol	Name
1.	BPBHPP	3(4'-bromophenyl)-4-benzoyl 5(2-hydroxyphenyl) pyrazole
2.	CPBHPP	3(4'-chlorophenyl)-4-benzoyl 5(2-hydroxyphenyl) pyrazole
3.	HPPCPD	1(2'-hydroxyphenyl)-2(2''-pyilidene) 3(2'-chlorophenyl) 1,3 dione
4.	HPMBPD	1(2'-hydroxyphenyl)-2(4''-methoxybenzylidene) 3-phenyl 1,3 dione
5.	η_l	Viscosity of liquid
6.	η_w	Viscosity of water
7.	η_{sp}	Specific Viscosity
8.	η_r	RelativeViscosity
9.	n	Refractive Index
10.	R_M	Molar Refraction
11.	d	Density of solution
12.	M	Molecular weight of ligand
13.	No	Avogadro's number
14.	α	Polarizibility constant

REFERENCES

[1] KJ Patil; SM Manwatkar and SS Donge. *Indian J. Chem.*, **1994**, 33, 4.
[2] RK Wadi and V Kakkar. *Indian J.Chem.*, **2000**, 39, 598.
[3] SS Joshi; TM Aminabhavi; RH Balundgi and SS Shukla. *J.Chem.Inorg.Data*, **1990**, 35, 1185.
[4] TM Aminabhavi; SS Joshi and SS Shukla. *Can.J.Chem.*, **1990**,68, 319.
[5] MI Aralaguppi; TM Aminabhavi; RH Balundgi and SS Joshi. *J.Phy Chem.*, **1991**, 96, 5299.
[6] SS Yadav. *Indian J.Chem.*, **1995**, 34, 131.
[7] BK Kalra; KC Singh and U Bhardwaj. *Indian J.Chem.*, **1994**, 33, 314.
[8] JD Pandey; GP Dubey; BP Shukla and SN Dubey. *Indian Chem.Soc.*, **1992**, 69, 750.
[9] BR Raut and I Chakravarty. *Indian J. Chem.*, **1994**, 33, 303.
[10] KN Mehrotra; K Tandon and MK Rawat. *J. Ind.Chem.Soc.*, **1992**, 69, 193.
[11] S Das and D Hazra. *Indian J. Chem.*, **1988**, 27, 898.
[12] UP Kapadi; PP Hankare and SK Chavan. *J. Ind.Chem.Soc.*, **1994**, 72, 269.
[13] G Jones and M Dole. *J.Am.Chem.Soc.*, **1929**, 51, 2950.
[14] Breslan BR and JF Miller. *J.Phys. Chem.*, **1970**, 74, 1956.
[15] V Vand. *J.Phys.Colloid.Chem.*, **1948**, 52, 277.
[16] RB Barry and FM Irving. *J.Phys.Chem.*, **1969**, 73, 2060.
[17] JD Pandey; A Yasmin and AK Sharma. *Indian J. Chem.*, **1998**, 37A, 1094.
[18] O Prakash; A Shrivastava and S Prakash. *Indian J .Pure Appl.Phys.*, **1986**, 24, 306.
[19] SK Rankar; TM Aminabhavi; SB Harogoppad and RH Baundgi. *Indian J.Tech*, **1993**, 31, 581.
[20] VP Kapila; CM Gupta and SP Jauhar. *Indian J. Chem.*, **1991**, 30, 711.
[21] SL Ostwal and MV Rathnam. *Indian J. Chem.*, **1987**, 26, 29.
[22] BG Khobragade and ML Narwade. *Acta Ciencia Indica*, **1983**, IX-c, 32.
[23] PB Agrawal and ML Narwade. *Indian J. Chem.*, **2003**, 42-A, 1047.

[24] JD Mahale; SC Manoja; NG Belsare and PR Rajput. *Ind. J. Chem.*, **2010**, 29 B, 505.
[25] VS Jamode; JC Dadhichi; DD Malkhede and ML Narwade. *J.Ind.Coun.of Chemist*, **2005**, 22-2, 35.
[26] BG Khobragade; ML Narwade; M Raffique and NS Quazi. *Act.Cien.Ind.*, **2007**, 33-c, 2, 113.